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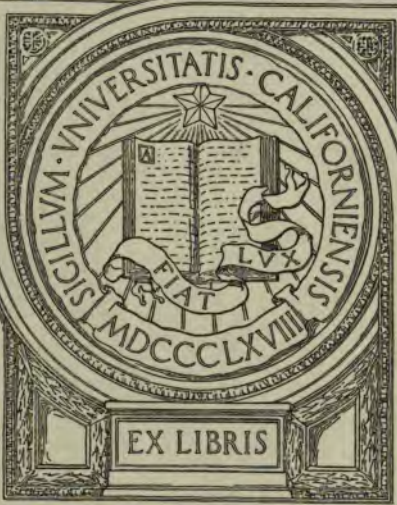
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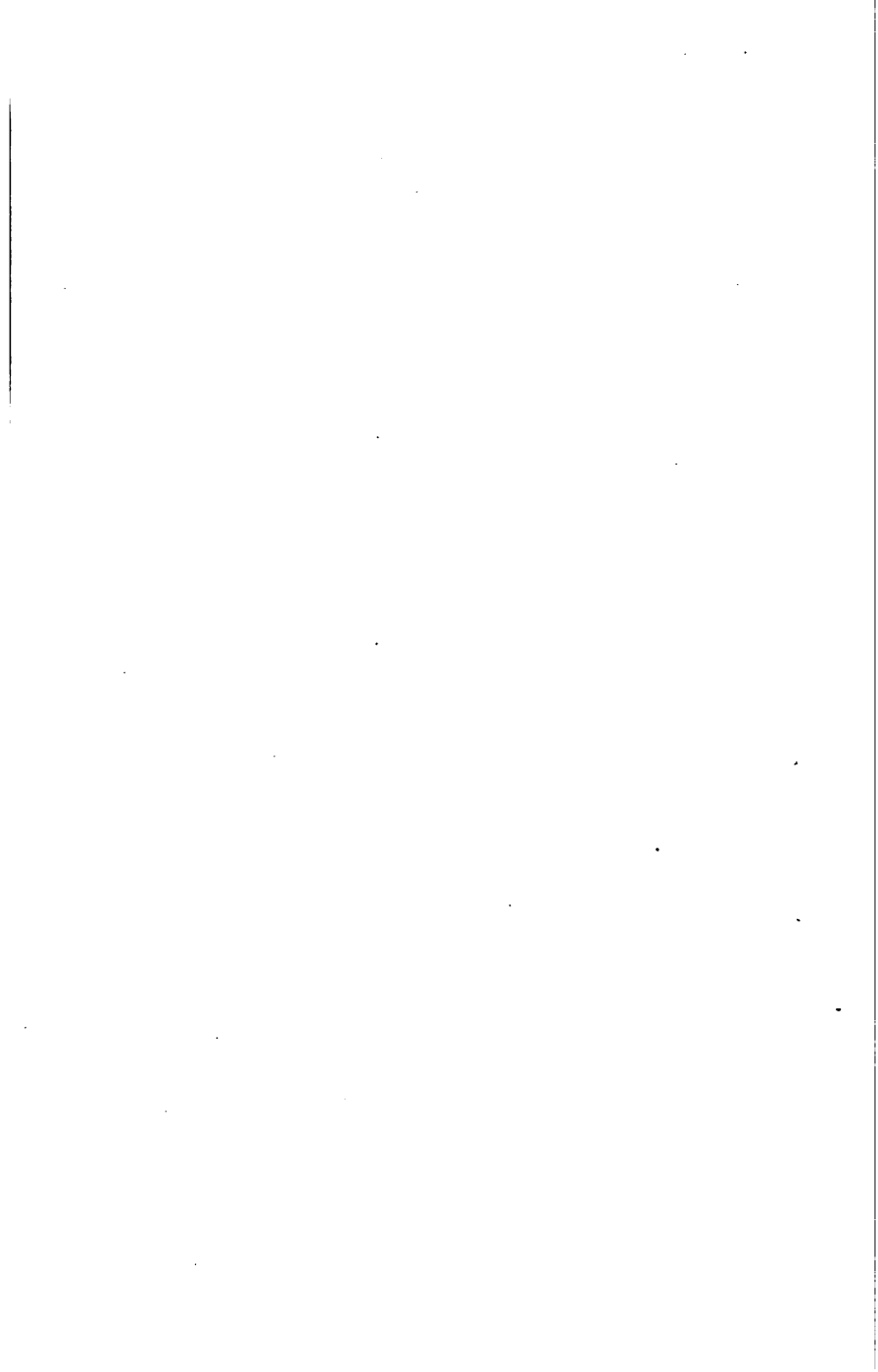
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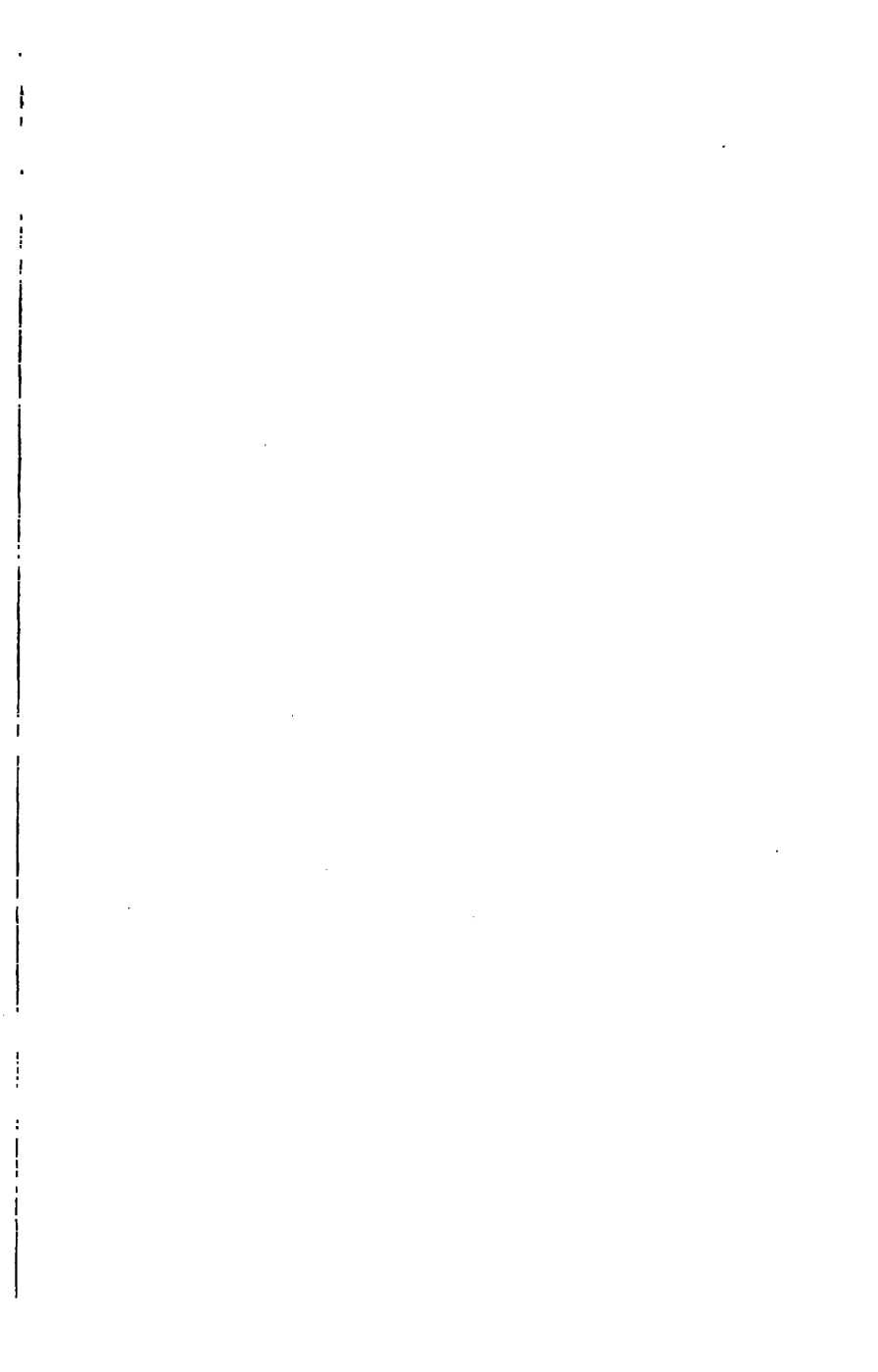
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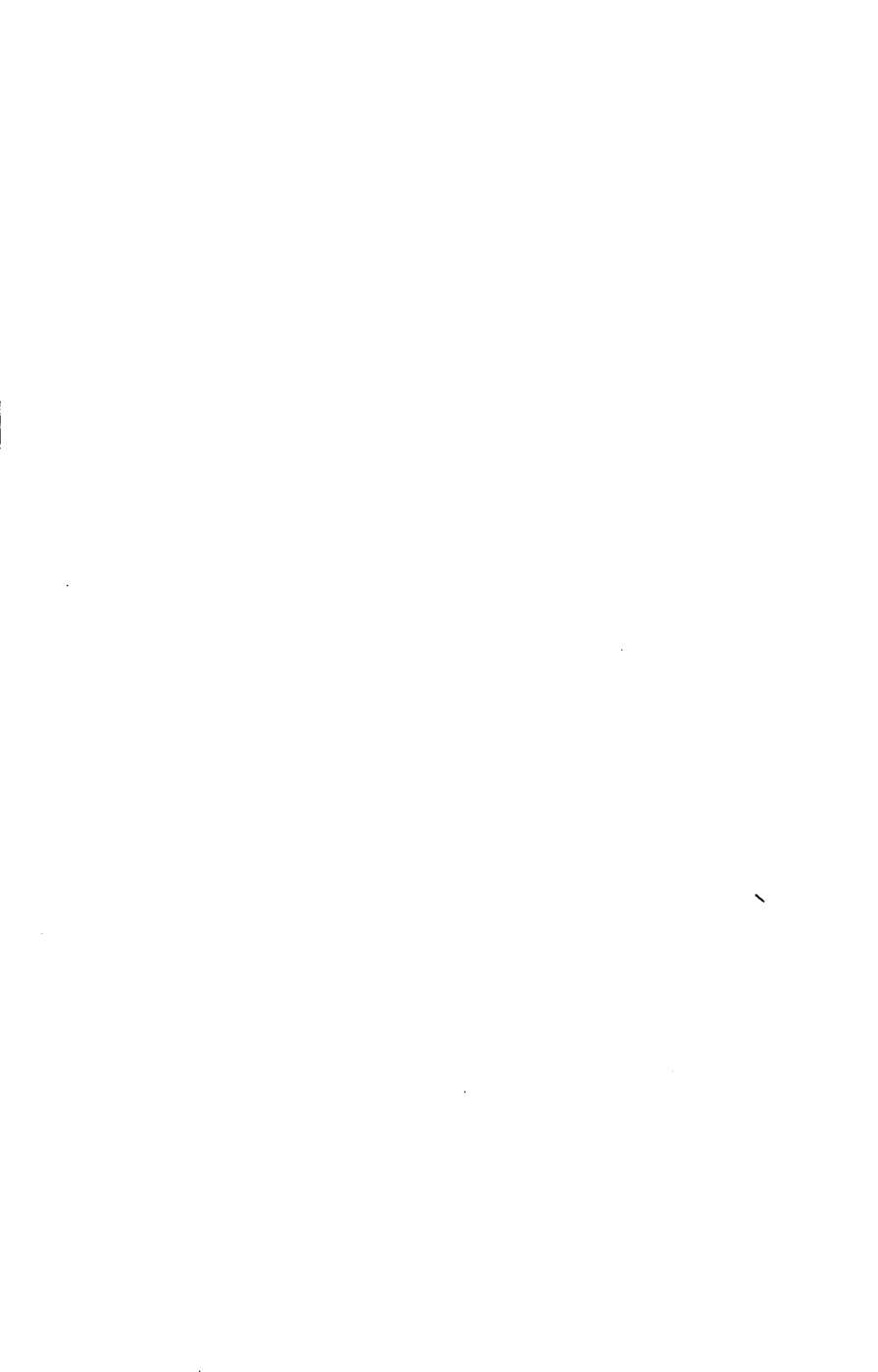


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CHEMISTRY

FOR SCHOOLS

BY

LOUIS SHERMAN DAVIS, Ph.D.

ASSOCIATE PROFESSOR OF CHEMISTRY, INDIANA UNIVERSITY

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PREFACE

Since school chemistry is essentially the interpretation of selected experimental data it cannot be taught successfully without a reasonably well-equipped laboratory. The educational value of experimental chemistry is greatly increased if many of the experiments are quantitative. Frequently the question is asked whether quantitative experiments in general chemistry have any place in secondary schools. The chief objections made are that such experiments take too much time and are too difficult for beginners. The time given to any experiment is never too much if that experiment is fundamental in developing a clear notion of the general principles of chemistry. Is it so much more difficult to weigh accurately than to solve quadratic equations, or to measure exactly than to demonstrate the Pythagorean theorem? The replies to nearly three hundred circular letters sent to teachers of chemistry in secondary schools, show that about ninety-five per cent believe in quantitative experiments.

Part I of this book is the study of theoretical chemistry. In arrangement the aim has been to follow the order of development of the science. In this way the truths of chemistry do not appear to be a series of unrelated facts, but a science whose new truth at each step seems naturally related to what has preceded. The titles of chapters will show the order of treatment:—States of Matter, Physical and Chemical Change, leading up to the atomic theory; The Essential Properties of Atoms, treating of the preparation of simple and compound gases, and the general properties of gases; The Determination of Atomic Mass, in order to develop a rational basis for a belief in specific atomic weights; The Determination of Formulas, about which

are grouped: (1) The relation of the density of a gaseous element to its atomic weight; (2) Density and molecular weight; (3) Density and the "two-volume law"; (4) Density and Avogadro's law; (5) Avogadro's law and formulas; (6) etc.; Formulas and Definite Proportions, with the method of reducing gas volumes to N. T. P.; Formulas and Multiple Proportions, for developing valence, and equivalent quantities; Relation of Valence to Oxidation and Reduction, discussing variation in valence, oxidizing and reducing agents, and the industrial applications of oxidation and reduction; Oxidation, Acids and Bases, with a study of allotropy, Raoult's law, and the origin of acid and alkaline oxides; Structure of Metallic and Non-metallic Oxides, developing the general formulas for acids and alkalis and explaining the chemical changes in neutralization and substitution; The Conservation of Energy in Chemical Reactions, as a basis for the study of chemical affinity.

The experiments were selected both for their simplicity and for their value in developing a general notion of the subject. It may not be advisable under all circumstances that all of the experiments shall be performed by the students. Under such circumstances the teacher should perform, in the presence of the class, those experiments which the pupils omit. Part or all the following experiments may be so treated:—15, 16, 21, 26, 31, 32, 34, 40, 46, 61, 67. Others which consume considerable time may be assigned to groups of students, each group reporting its results to the class for general interpretation; e.g., experiments 34, 35, 46, 51, 52, 53, 55, 69.

The general notion about which all of the material in Part II is grouped, is the periodic law. In developing the basis for interpreting the periodic law, nine groups of elements are discussed. In studying the chief characteristics of each group the hydrogen, halogen, and oxygen derivatives are used. By this treatment of the attributes of these three types of derivatives the mutual relations of the groups are brought out. As

many industrial processes are discussed as are consistent with the scope of the book, because it is one of the chief functions of chemistry in secondary schools to enrich the life of the student by enabling him to put a large content into the objects and processes which contribute so much to his everyday life.

The descriptive matter under the carbon group (p. 244), especially that which outlines the fundamental chemical and physical properties of fats, starch, sugar, albumens, etc., is intended to supply supplementary material for work in physiology. The chapter on chemistry and life is designed to give the student a comprehensive view of the transformation of energy and its relation to life.

The atomic weights used in Part I are approximate in order that they may be more easily remembered. Thus, in experiment 55, page 166, the atomic weight of silver is given as 107, although the exact weight is 107.93. Most of the illustrations are suggestive, rather than exact reproductions of the object or apparatus. Thus, Figure 49, page 210, is far from a technical representation of a sulphuric acid plant; it is used because it enables the student to trace the fundamental chemical changes in making sulphuric acid.

I take pleasure in expressing my gratitude to Dr. F. M. Andrews of Indiana University for his helpful criticisms, especially on the chapter relating to photosynthesis and the nitrification of complex nitrogenous compounds.

L. S. D.

BLOOMINGTON, INDIANA, June, 1904.



TABLE OF CONTENTS

CHAPTER I

	PAGE
STATES OF MATTER—PHYSICAL AND CHEMICAL CHANGE.....	11
Definition of Chemistry—Essential Properties of Iron— The Essential Properties of Lead—Homogeneity is Independent of Mass—Mass and Mechanical Subdivision—Mass and Chemical Subdivision—Significance of Chemical Subdivision—Chemical Change and the Atomic Theory—Analytic and Synthetic Changes—Physical and Chemical Changes Compared.	

CHAPTER II

THE ESSENTIAL PROPERTIES OF SIMPLE AND COMPOUND GASES...	23
Properties of Atoms—Properties of Hydrogen—Some Acids contain Hydrogen—Preparation of Oxygen—Properties of Oxygen—Occurrence of Oxygen—Preparation of Hydrogen Sulphide—Composition of Hydrogen Sulphide—Properties of Hydrogen Sulphide—Occurrence of Hydrogen Sulphide—Preparation and Properties of Carbon Dioxide—Preparation of Relatively Pure Carbon—Properties of Carbon—Varieties of Carbon—Preparation and Uses of Amorphous Carbon—The Combustion of Carbon in Oxygen—Carbon in Carbon Dioxide—Composition of Carbon Dioxide—The Physical Properties of Gases—Relation of Pressure to Volume—Mass and Density—Relation of Volume and Temperature.	

CHAPTER III

THE DETERMINATION OF ATOMIC MASS.....	44
The Electrolysis of Water—Composition of Water by Volume—Determination of the Atomic Weight of Oxygen—The Atomic Weight of Copper—Specific Atomic Weights.	

CHAPTER IV

THE DETERMINATION OF FORMULAS.....	PAGE 54
------------------------------------	------------

Properties of Chlorine—Commercial Value of Chlorine—The Action of Chlorine on Hydrogen—Properties of Hydrogen Chloride—Determination of the Formula of Hydrogen Chloride—Preparation of Iodine—Properties of Iodine—Hydrogen Iodide—Preparation of Nitrogen—Properties of Nitrogen—The Relation of Nitrogen to Life—Composition of the Air—Preparation of Ammonia—Properties of Ammonia—Composition of Ammonia—The Relation of the Density of a Gaseous Element to its Atomic Weight—Density and Molecular Weight of an Elementary Gas—Density and Molecular Weight of a Compound Gas—Density and the “Two Volume Law”—Density and Avogadro’s Law—Avogadro’s Law and Formulas—The “Two Volume Law” and the Molecular Theory of Gases—The Molecular Theory of Gases and “Nascent Elements”—Nascent Elements and Ozone—Preparation of Ozone—Ozone is a Form of Modified Oxygen—Structure of Ozone.

CHAPTER V

FORMULAS AND DEFINITE PROPORTIONS.....	86
--	----

The Deportment of Magnesium toward Hydrogen Chloride—The Electrolysis of Water and Definite Proportions—Composition of Ammonia and Definite Proportions.

CHAPTER VI

FORMULAS AND MULTIPLE PROPORTIONS.....	91
--	----

The Combination of Silver and Chlorine in Definite Proportions—The Combination of Silver and Sulphur in Definite Proportions—Combination in Definite Proportions—Elements Combine in Definite and Multiple Proportions—Multiple Proportions and Valence—Valence and the Structure of Molecules—Variation in Valence—Valence and Compounds—Valence and Equivalent Quantities.

CHAPTER VII

THE RELATION OF VALENCE AND MULTIPLE PROPORTIONS TO OXIDATION AND REDUCTION.....	107
--	-----

Oxidation—The Relation of Oxidation to Valence—Reduction—The Relation of Reduction to Valence—The Gas Flame as an Oxidizing and a Reducing Agent—Oxidation and Reduction in the Preparation of Iron and Steel—Preparation of Wrought Iron.

CHAPTER VIII

	PAGE
BASES AND ACIDS	122

Preparation of Sulphur—Properties and Uses of Sulphur—Allotropic Forms of Sulphur—Allotropy and the Constitution of Gaseous Molecules—Allotropy and the Weight of Molecules of Solids—Preparation of Phosphorus—Properties—Red Phosphorus—The Combustion of Phosphorus in Oxygen—The Combustion of Sulphur in Oxygen—The Combustion of Sulphur Dioxide in Oxygen—Carbon Dioxide in Water—Properties of the Oxides of Sulphur, Phosphorus, and Carbon—Preparation of Sodium—Properties of Sodium—Properties of Potassium—Preparation and Properties of Magnesium—Preparation and Properties of Calcium—Oxidation of Metallic Sodium—Oxidation of Metallic Potassium—Oxidation of Magnesium—Oxidation of Calcium—Preparation of Calcium Oxide from Calcium Carbonate—The Solution of the Metallic Oxides in Water—Properties of Barium—Preparation and Properties of Strontium—Preparation of Barium and Strontium Hydroxides—The Alkaline Hydroxides—The Acid Hydroxides—The Oxides of Nitrogen.

CHAPTER IX

THE STRUCTURE OF METALLIC AND NON-METALLIC OXIDES	150
--	-----

The Deportment of Acids toward the Electric Current—The Deportment of the Alkalis toward the Electric Current—General Structure of Acid and Alkaline Hydroxides—Preparation of Materials—The Electrolysis of a Copper Compound—The Electrolysis of Alkali and Alkali-Earth Compounds—Neutralization—A General Formula for Neutralization—Neutralization and Acids, Bases, and Salts—The Naming of Acids, Bases, and Salts—Substitution—Bases and Hydroxides Compared.

CHAPTER X

THE CONSERVATION OF ENERGY IN CHEMICAL REACTIONS	174
---	-----

Energy Defined—Energy Transformed—Selective Energy—Energy in Molecules—Energy Expressed—Photosynthesis—The Purpose of Photosynthesis—Endothermic Compounds and Foods—Stability of Exothermic and Endothermic Compounds—Electrolysis of Exothermic Compounds—Dissociation—Dissociation, and the Theory of Electrolysis.

CHAPTER XI

PAGE

THE HALOGEN GROUP OF ELEMENTS: GROUP I..... 191

Properties of Fluorine—Hydrofluoric Acid—Salts of Hydrofluoric Acid—Oxygen Derivatives of Chlorine—Salts of Hypochlorous Acid—Properties of Bleaching Powder—Bleaching Cotton and Linen Fabrics—Chlorine Dioxide—Properties of Chlorine Dioxide—Chloric Acid—Salts of Chloric Acid—Perchloric Acid—Preparation of Bromine—Properties of Bromine—Hydrogen Bromine—Oxygen Derivatives of Bromine—Iodine Pentoxide—Iodic Acid—Periodic Acid.

CHAPTER XII

THE OXYGEN GROUP OF ELEMENTS: GROUP II..... 204

Hydrogen Derivatives of Sulphur—Halogen Derivatives—Oxygen Derivatives—Sulphurous Acid—Salts of Sulphurous Acid—Sulphuric Acid—Preparation of Sulphuric Acid—Properties of Sulphuric Acid—Salts of Sulphuric Acid—Properties of Selenium—Hydrogen Selenide—Halogen Derivatives—Oxygen Derivatives—Hydrogen Telluride—Halogen Derivatives—Oxygen Derivatives—Tellurous Acid—Telluric Acid—Comparison of Halogen and Oxygen Groups.

CHAPTER XIII

THE NITROGEN GROUP OF ELEMENTS: GROUP III..... 219

Hydrogen Derivatives of Nitrogen—The Manufacture of Artificial Ice—Chemical Properties of Ammonia—Salts of Ammonia—The Halogen Derivatives of Nitrogen—Oxygen Derivatives of Nitrogen—Nitrous Acid—Salts of Nitrous Acid—Nitric Acid—The Action of Nitric Acid on Metals—Salts of Nitric Acid—Black Gunpowder—Preparation and Uses of Phosphorus—Hydrogen Derivatives—Chemical Properties of Phosphine—Halogen Derivatives—Oxygen Derivatives of Phosphorus—Phosphorous Acid—The Phosphoric Acids—Orthophosphoric Acid—Salts of Phosphoric Acid—Metaphosphoric Acid and its Salts—Properties of Arsenic—Hydrogen Derivatives—Halogen Derivatives—Oxygen Derivatives—Arsenious Acid—Arsenic Acid—Preparation and Properties of Antimony—Hydrogen Derivatives—Halogen Derivatives—Oxygen Derivatives—Preparation and Properties of Bismuth—Halogen Derivatives—Oxygen Derivatives—Salts of Bismuth.

CHAPTER XIV

	PAGE
THE CARBON GROUP OF ELEMENTS: GROUP IV	244

Carbon and Silicon—Calcium Carbide—Hydrogen Derivatives—Methane and Other Fuels—Preparation of Illuminating Gas—Illuminating Gas by Dissociation of Steam—Composition of Coal and Water Gas—Properties of Illuminating Gas—Coal Tar—Halogen Derivatives of Carbon—Oxygen Derivatives—Carbonic Acid—Effervescing Waters—The Leavening Process—Sulphur Derivatives of Carbon—Sulphocarbonic Acid—Cyanogen—Hydrogen Cyanide—Ethane, Propane, etc.—Petroleum and Its Products—Monatomic and Diatomic Alcohols—Triatomic Alcohols—Properties of Aldehydes—Formaldehyde—Chloral—Chloral Hydrate—Composition of Organic Acids—Acetic Acid—Preparation of Vinegar—Salts of Acetic Acid—Palmitic Acid—Stearic Acid—Oleic Acid—Composition of Fats—Butter—Oleomargarine—Soap—Preparation of Soap: Laboratory Method—Preparation of Soap: Commercial Method—Composition of Carbohydrates—Properties of the Carbohydrates—Sugar-Making—Properties of Grape Sugar—Starch—Starch and Malted Foods—Baby Foods—Cellulose—Uses of Cellulose—Paper-Making—Modifications of Cellulose—Properties of Guncotton—Properties of Albumens.

CHAPTER XV

THE CARBON GROUP (Continued)	292
------------------------------------	-----

Occurrence of Silicon—Preparation and Properties of Silicon—Silicon Hydride—Halogen Derivatives—Oxygen Derivative—Properties of Silicon Dioxide—Silicic Acid—Silicates—Uses of Silicon Dioxide and the Silicates—Other Compounds of Silicon.

CHAPTER XVI

THE CARBON GROUP (Continued)	301
------------------------------------	-----

Lead and Tin—Occurrence and Preparation of Lead—Properties of Lead—Uses of Lead—Halogen Derivatives—Oxygen Derivatives—Salts of Lead—Paints and Painting—Occurrence and Preparation of Tin—Properties of Tin—Uses of Tin—Halogen Derivatives.

CHAPTER XVII

	PAGE
THE BORON GROUP OF ELEMENTS: GROUP V	313
Properties of Groups I, II, and III—General Properties— Occurrence of Boron—Properties of Boron—Hydrogen Deriva- tives—Halogen Derivatives—Oxygen Derivative—Boric Acid—The Borates—Occurrence of Aluminium—Preparation of Aluminium by Electrolysis—Properties of Aluminium— Uses of Aluminium—Halogen Derivatives—Oxygen Deriva- tive—Aluminium Hydroxide—Other Compounds of Alu- minium—Salts of Aluminium—Alums—The Silicates of Alu- minium—Kaolin—Porcelain—Stoneware—Earthenware— Bricks—Ultramarine.	

CHAPTER XVIII

THE CHROMIUM GROUP: GROUP VI	330
General Properties of Group VI—Occurrence of Chro- mium—Properties of Chromium—Halogen Derivatives—Oxy- gen Derivatives—Salts of Chromic Acid—Properties of a Mordant—Use of a Mordant in Pattern-Making—Chemical Character of Chromium—Occurrence and Preparation of Manganese—Properties of Manganese—Halogen Derivatives— Properties of the Permanganates—Uses of the Permanganates —Chemical Character of Manganese—Chemical Character of Oxides Compared.	

CHAPTER XIX

THE ALKALI-EARTH GROUP: GROUP VII	340
General Properties of Sub-Group A—Halogen Derivatives of Magnesium—Oxygen Derivatives—Other Salts of Magne- sium—Occurrence and Preparation of Zinc—Properties of Zinc—Uses of Zinc—Halogen Derivatives—Oxygen Deriva- tive—Salts of Zinc—Properties and Uses of Cadmium—Occur- rence and Preparation of Mercury—Properties of Mercury— Uses of Mercury—Halogen Derivatives—Oxygen Derivatives— Other Compounds of Mercury—Sub-Group A—General Char- acter of Sub-Group B—Halogen Derivatives of Calcium— Oxygen Derivatives—Calcium Monoxide—Slaked Lime: Cal- cium Hydroxide—Mortar—Cements—Other Compounds of Calcium—Preparation of Acetylene—Properties of Acetylene— Halogen Derivatives of Barium—Oxygen Derivatives— Properties and Uses of Strontium—General Properties of the Alkali-Earth Family.	

CHAPTER XX

PAGE

THE ALKALI GROUP OF ELEMENTS: GROUP VIII.....	359
--	------------

The Relation of Group VIII to the Preceding Groups—
General Properties of Sub-Group A—Occurrence and Properties of Lithium—Preparation of Sodium—Preparation and Properties of Sodium Hydroxide—Preparation of Sodium Carbonate—Properties of Sodium Carbonate—Sodium Bicarbonate—Preparation and Properties of Potassium—Halogen Derivatives—Other Salts of Potassium—Rubidium and Caesium—Occurrence and Properties.

CHAPTER XXI

Group VIII (Continued)	368
-------------------------------------	------------

Sub-Group B: Copper, Silver, and Gold—General Properties—Occurrence of Copper—Preparation of Copper—Electrolytic Purification of Copper—Properties of Copper—Uses of Copper—Halogen Derivatives—Oxygen Derivatives—Salts of Copper—General Processes in Electroplating—Occurrence and Preparation of Silver—Properties of Silver—Uses of Silver—Alloys of Silver—Halogen Derivatives—Photography—Oxygen Derivatives of Silver—Salts of Silver—Occurrence and Preparation of Gold—Properties of Gold—Uses of Gold.

CHAPTER XXII

THE IRON GROUP OF ELEMENTS: GROUP IX.....	384
--	------------

General Properties—Preparation—Halogen Derivatives—Hydroxyl Derivatives—Cyanogen Derivatives—Oxygen Derivatives—Salts of Iron—Sulphur Derivatives—Occurrence and Properties of Nickel—Alloys of Nickel—Halogen Derivatives—Oxygen Derivatives—Cyanogen Derivatives—Properties of Cobalt—Compounds of Cobalt—Halogen Derivatives—Oxygen Derivatives—Cyanogen Derivatives—Other Compounds—The Iron Family.

CHAPTER XXIII

CLASSIFICATION OF ELEMENTS	391
---	------------

Metals, Non-Metals, and Metalloids—The Law of Octaves—The Periodic Law—The Gaps in the Periods—Uses of the Periodic Law.

CHAPTER XXIV

CHEMISTRY AND LIFE	PAGE 398
Elements Necessary to Plant-Life—Sources of Nitrogen— The Rotation of Nitrogen.	

APPENDIX

The Thermometer—A Water-Bath—Drying Oven—Pneumatic Trough—A Gasometer—Measuring Liquids—Weighing Solids—Hydrogen Sulphide or Hydrogen Generator—Glass Tubes—Cork Stoppers—Filtering—Evaporating—Distilling—Fusion—Preparation of Copper Oxide—To Graduate a Glass Tube—To Prepare an Electromagnet—Quantitative Relation of Pressure to the Volume of a Gas—To Ascertain the Volume of a Gas at 0° Temperature—To Ascertain the Volume of a Gas at 760 mm. Pressure—To Ascertain the Volume of a Gas at 0° Temperature and 760 mm. Pressure—To Prepare Starch-Paste—Preparation of Sulphur Trioxide—To Prepare a Standard Solution of Oxalic Acid—To Prepare a Standard Solution of Sodium Hydroxide—To Prepare an Ammonia-Silver Solution—Table of Atomic Weights	408
INDEX.	419

CHEMISTRY

CHAPTER I

STATES OF MATTER—PHYSICAL AND CHEMICAL CHANGE

1. Definition of Chemistry.—Modern life is richer than that of the ancients, partly because it has at command a great variety of substances which modern science has created from the primitive materials which nature supplies.

Although the ancients held the belief that the substances which occur in the earth are made up of different kinds of very minute particles, yet, until the development of chemistry, people depended wholly upon the resources of nature. That which did not exist ready formed did not exist at all. Natural substances, such as limestone, coal, flint, water, air, clay, and wood were well known to our ancestors, but of such products as chloroform, ether, quinine, soap, aniline dyes, steel, and porcelain, they had no knowledge. Some of these things were doubtless discovered by chance, but many are the result of patient research. Modern chemistry, in short, has discovered processes by which many of the substances our ancestors knew can be transformed into other and more useful forms. Chemistry may, therefore, be defined as the science which deals with the composition of various kinds of substances, and with the transformation of their constituents into other forms and combinations.

The experiments in the succeeding pages show how some of these transformations may be brought about.

2. Essential Properties of Iron.—EXPERIMENT 1. Clean a piece of ordinary iron wire with sandpaper, and observe its physical properties, that is, the attributes which together serve to distinguish it from all other substances. These attributes give it *homogeneity*. It is essential that this term be clearly understood. A ton of pure sugar is homogeneous, for even the smallest part of it is sugar, possessing the attributes of the whole. But a barrel of sand which contains a grain of sugar is not a homogeneous mass, for all of its particles have not the same qualities. A substance, then, is said to possess homogeneity when *any* part of it possesses *all* the attributes of the whole. Homogeneity, therefore, is perfect uniformity. We select definite attributes which distinguish iron from all other familiar substances. Since it is a heavy metal of grayish color, hard and ductile, i.e., capable of being drawn into wire, and readily attracted by a magnet, we may select as attributes by which to identify it: (1) high specific gravity, (2) grayish color, (3) notable hardness, (4) ductility, and (5) magnetic character.

File the piece of iron wire, and examine the attributes of the fine powder as above directed. Is it magnetic? Does every fractional part of it possess this attribute? Is it homogeneous? Is every particle iron?

3. The Essential Properties of Lead.—EXPERIMENT 2. Clean a piece of lead by scraping it with a knife-blade or sandpaper. The attributes which serve to establish its identity are: (1) its grayish-white color, (2) its softness, (3) its malleability, which may be readily shown by placing a small piece of lead on the bottom of an inverted mortar, and striking it vigorously several times with a pestle, and (4) its low

melting point. Place a bit of lead on a piece of charcoal or in a porcelain crucible, cover it with a little sodium carbonate to exclude the air, and expose it to a blow-pipe or a bunsen gas flame. The lead will melt quickly. These attributes establish the identity of lead.

File a piece of lead and examine the properties of the filings. Is each particle lead? Does the smallest part possess the same attributes as the whole? From the experiments it is apparent that when such substances as iron and lead are finely divided by some mechanical means, such as filing or scraping, the particles, however small, possess the attributes of the original material; in other words, the original material retains its homogeneity because no part has lost any of the essential attributes of the whole.

4. Homogeneity is Independent of Mass.—That homogeneity is independent of mass or quantity may be illustrated with common table salt. Select a pure sample. It is popularly known by (1) its peculiar salty flavor, (2) its ready solubility in water, and (3) its cube-shaped crystals. It may be characterized by two other attributes, brought out by Experiment 3.

EXPERIMENT 3. Dissolve about 1 gm. of salt in 10–20 cubic centimeters (cc.) of water, dip a clean platinum wire into the solution, and then thrust it into the outer zone of a colorless bunsen (see p. 111) or alcohol flame; it will impart (4) a brilliant yellow color to the flame. Put a drop of the salt solution into a test tube, add 5–10 cc. of distilled water, and then about ten drops of silver nitrate solution (1:20). (5) A white precipitate will be formed, or, if there was very little salt, an opalescent color will appear in the fluid in the tube. These five tests will serve at present to identify salt. Pulverize about 2 gm. of common salt, place the powder in a small porcelain crucible, rest the crucible in a wire triangle

(B, Fig. 1) supported by a ring-stand A, and heat it for five minutes in a small colorless bunsen or alcohol flame. Then let it cool, and weigh out accurately (see Appendix) 1 gm.

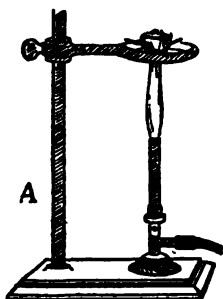
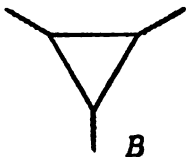


FIGURE 1



of the dried powder, and transfer it, without loss, to a 500 cc. graduated flask, Fig. 2. This may be done as follows: Place a small funnel in the neck of the flask, and by means of a feather or camel's hair brush transfer every particle of the salt from the

paper or glass on which it was weighed, into the funnel. Dissolve the salt in distilled water, rinse the funnel carefully five or six times, remove it, and fill the flask with distilled water until the bottom of the meniscus, M, Fig. 2, coincides with the mark N, and shake thoroughly. It is essential to the success of this experiment that the liquid be thoroughly mixed.

Select a clean evaporating dish about 7 cm. in diameter, support it on a clean triangle and ring-stand (see Fig. 1), heat it two or three minutes in a colorless flame, place the dish while hot in a desiccator*, let it cool, and weigh it.

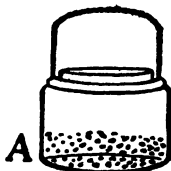


FIGURE 3

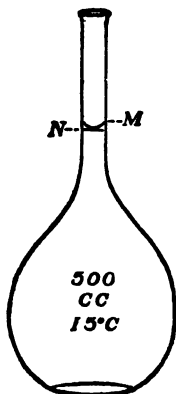


FIGURE 2

Measure accurately into the weighed porcelain dish 25 cc. of the salt solution prepared

*A convenient form of desiccator is shown in Fig. 3. The bottom is covered to a depth of 5 cm. with fused calcium chloride, A. This substance absorbs water readily, thereby securing a perfectly dry air in the closed vessel. When a hot dish is put in the desiccator and the lid securely placed, it will cool in this dry air without condensing any moisture upon its surface.

as above, evaporate it to dryness on a water-bath, and at a temperature of 100° C. dry the whole until constant weight is obtained, i.e., until the dish and contents cease to lose weight on being reheated to 100° . The dish should be allowed to cool in the desiccator before each weighing. The increase in weight over the weight of the dried dish represents the quantity of salt which was contained in 25 cc. of the original solution.

Why would not the cloth-dried dish have sufficed for this experiment? What fractional part of the 1 gm. does this dried quantity represent? Why was the original 2 gm. of salt dried so thoroughly before weighing out the 1 gm. for solution in 500 cc. of water?

Repeat the experiment, using 50 cc. of the salt solution. What part of the original gm. does the result represent?

If the experiments were accurately carried out, the weight of salt in 25 cc. of the solution was approximately 0.05 gm.; that in 50cc. was about 0.1 gm. If your results do not agree with these figures, repeat the experiments until the source of error is discovered.*

Interpretation:

25 cc. = $\frac{25}{500} = \frac{1}{20}$ of the original solution.

0.05 gm. = quantity of salt found in 25 cc. = $\frac{1}{20}$ of the original gm.

50 cc. = $\frac{50}{500} = \frac{1}{10}$ of the original solution.

0.10 gm. = quantity of salt found in 50 cc. = $\frac{1}{10}$ of the original gm.

These results show that $\frac{1}{20}$ of the original solution contained $\frac{1}{20}$ of the salt, while $\frac{1}{10}$ of the solution contained $\frac{1}{10}$ of the salt. We conclude, therefore, that in a thoroughly mixed solution of common salt, the salt is uniformly diffused. In general we may say that any substance which dissolves completely in a liquid, diffuses uniformly through it. This law is of the greatest value

* Sufficient skill to enable the student to weigh and measure quantities without error is acquired only with much practice and great care. The acquisition of such skill is absolutely essential to further progress.

to the chemist, since it enables him to determine extremely small quantities. Thus, if a solution of 500 cc. contains 1 gm. of salt, 1 cc., or $\frac{1}{500}$ of the original volume, will contain $\frac{1}{500}$ of 1 gm. Similarly 0.1 cc., or $\frac{1}{5000}$ of the original volume, will contain $\frac{1}{5000}$ of 1 gm., etc. Measure out 0.1 cc. of the original salt solution prepared as above, dilute it to exactly 100 cc. with distilled water, mix well, and examine 0.05 cc. of this solution for the presence of salt as directed in Experiment 3. The tests with platinum wire and silver nitrate should give distinct results. How much salt was contained in this 0.05 cc. used for the examination?

Calculation:

500.0 cc. of the liquid contained	1.0000	gm. salt.
0.1 cc. " " "	.0002	" "
0.1 cc. diluted to 100 cc. "	.0002	" "
0.05 cc. of this diluted solution contained	.000001	" "

This one-millionth of a gm. is inconceivably small; it could not be detected by the most accurate balances; it would not be visible to the naked eye, yet it possesses all the attributes of the original gm. It is as truly representative of common salt as an inconceivably large quantity would be. Homogeneity is independent of mass.

5. Mass and Mechanical Subdivision.—The power of certain substances to retain their homogeneity after minute subdivision may be still more strikingly illustrated as follows: Place 1 gm. of musk on a glass plate, in a room of large dimensions, e.g., $40 \times 40 \times 20$ feet, and let it evaporate. After a few hours, the smallest part of the air in the room will be found impregnated with the odor. This can only mean that each cubic inch contains a detectable quantity of the original substance. The law of diffusion holds for gases

as well as for liquids. A little calculation will reveal the minuteness of the subdivision of the musk:

$$40 \times 40 \times 20 = 32,000 \text{ cubic feet} = \text{contents of room.}$$

$$32,000 \text{ cubic feet} = 55,296,000 \text{ cubic inches.}$$

$$\frac{1}{55,296,000} \text{ gm. of musk in each cubic inch of space, if}$$

all the musk has been volatilized and if none of it has escaped from the room. No one can form any adequate notion of such a quantity. Other substances which lend themselves to equally minute subdivision and yet remain detectable might be selected. Such experiments lead to the conclusion that the essential attributes, and consequently the homogeneity, of many substances can not be changed by subdivision, however minute, through such means as powdering, dissolving, or vaporizing. Changes thus effected are physical, not chemical.

6. Mass and Chemical Subdivision.—EXPERIMENT 4.

Cover 1 gm. of finely divided lead with dilute nitric acid, heat it directly over a wire gauze until completely dissolved, filter off any foreign matter, and complete the evaporation to dryness on a water-bath. Spread the dry powder on a slip of clean blotting paper and examine it carefully with a lens. Does it appear to be homogeneous? Is it lead? Compare Experiment 2.

If it is homogeneous it must be an individual substance, possessing characteristic attributes. What are some of these attributes? Can it be pulverized? Can lead? Is it soluble in water? Is lead? Is it malleable? Is lead? Does it melt readily? Does lead? Does this new substance contain lead? This may be ascertained as follows:

Mix intimately about 0.5 gm. of the substance with twice its bulk of sodium carbonate, place a portion of the mixture on

a piece of charcoal, and expose it to the reducing zone of the blow-pipe (see p. 112). A sphere of lead will be obtained.

7. Significance of Chemical Subdivision.—Here we have a new situation—a homogeneous substance which possesses none of the attributes of lead, and yet contains lead. These facts indicate that the original substance, which possessed all the attributes of lead and served to identify it as such has formed a combination with the nitric acid, so intimate that the resulting compound acts like a homogeneous substance under such mechanical means of subdivision as trituration and solution. From the point of view of attributes it is a new substance, “a chemical individual.” A similar reaction is shown in Experiment 5.

EXPERIMENT 5. Place five short strips of thin copper cuttings in a small porcelain crucible, cover them completely with powdered sulphur, cover the crucible with a closely fitting lid, and heat it over a small flame for fifteen minutes. The flame should be only sufficient to keep the sulphur in a fluid state. Remove the crucible lid, heat the contents gently until all sulphur is expelled and the resulting mass is quite dry. Place the substance on a piece of clean white paper and examine its attributes.

If the experiment has been successfully carried out, the product will be found to possess the attributes neither of copper nor of sulphur. Does it contain copper? To answer this question place a sample of it in a porcelain dish, add 2 or 3 cc. of dilute nitric acid, and heat it gently until it is dissolved. A clean bright knife-blade placed for a moment in this solution will be coated with a thin layer of metallic copper. Since the new substance contains copper, it must be the product of an intimate union of copper and sulphur, for they were the only materials present in the crucible.

When two or more substances, each of which possesses

characteristic attributes, react upon each other so that one or all lose their attributes, the change is said to be a *chemical* one. The combination of lead and nitric acid, and the union of copper and sulphur are good examples. These changes must be chemical, for in each case the participating substances lose their characteristic attributes, and the result is a homogeneous substance, with attributes entirely distinct from those of the combined substances. The new substance cannot, therefore, be an intimate mechanical mixture of the combined substances. This view may be easily sustained, since a mixture of copper filings and sulphur, when triturated thoroughly, forms a greenish powder in which the pieces of unchanged copper may be readily seen. When, however, the mixture is strongly heated, it gives the results outlined in Experiment 5. In the first case the result is a *mechanical mixture*; in the second, a *chemical compound*. What is the essential difference between these two products? The interpretation of this difference involves the two most important theories of the ultimate constitution of matter.

8. Chemical Change and the Atomic Theory.—The Greeks advanced the theory that every substance is capable of *infinite* subdivision. To illustrate: In Experiment 1, we reduced some iron to an impalpable powder, and found that any portion of the powder retained all the attributes of the original substance, and was therefore only finely divided iron. In Experiment 3, we were able to subdivide 1 gm. of salt into 1,000,000 equal parts, each possessing the attributes of the whole. Again, by employing the diffusion of gases as a means of subdivision, we were able to divide 1 gm. of musk into at least 50,000,000 parts. Such experiments led to the belief that the limit to subdivision was not found in the substances themselves, but in the means used to effect that subdivision.

The second theory of the ultimate constitution of substances—also of Greek origin—was expounded by Dalton in 1810. He and his followers believed that substances are only *finely* divisible. That is to say, they believed that the limit to which a homogeneous substance may be divided, and yet retain its homogeneity, is grounded in the nature of the substance itself, and not in the means used to effect this subdivision. It is apparent that these views are diametrically opposed. In order to explain the finite divisibility of a substance, Dalton assumed that it is made up of individual units called atoms, or elements, which cannot be divided.

Let us interpret an experiment in terms of this theory. We learned that when a mixture of copper and sulphur is heated, a new substance is formed which is made up of copper and sulphur in intimate combination. The Dalton theory explains this combination by affirming that the individual units or “atoms” of the copper combine with like units of sulphur.

For the sake of illustration, let the spheres ● ● represent one atom of copper and one of sulphur respectively. These combine, according to Dalton’s theory, to form a new substance, which may be represented by the graph $\begin{matrix} \text{Cu} & \text{S} \\ \bullet & - & \bullet \end{matrix}$. (The symbols, Cu and S, placed above the spheres, denote respectively one atom of copper [cuprum] and one of sulphur.) Such a group is called a *molecule*. A molecule is the smallest particle of matter which can exist independently. There are molecules of simple substances or *elements*, and molecules of compound substances. The former are made up of atoms of the same kind; the latter of atoms of different kinds.

If Dalton’s theory, that all matter is made up of indivisible atoms, is correct, it follows that all matter is *indestructible*; for even if we employ any or all of the processes of subdivision, the atoms remain, though the substance acted upon loses all of its attributes. It follows, also, that the chemist cannot

create matter; the most that he can do is to bring about new combinations of the atoms of elements which already exist.

Dalton's theory has been accepted by modern chemists as affording a satisfactory basis for the explanation of the common chemical phenomena which have been studied by them. It should be borne in mind, however, that this theory, commonly designated "The Atomic Theory," is accepted only as a *working hypothesis*, not as a fact.*

9. Analytic and Synthetic Changes.—A chemical change, interpreted in terms of this hypothesis, may consist in (a) the intimate combination of two or more atoms or groups of atoms to form a new molecule; in (b) the separation of a molecule into the atoms or groups of atoms which compose it. The first process is constructive or synthetic; the second, destructive or analytic. There is a third type of chemical change which we are not yet prepared to interpret. It is both analytic and synthetic, and is one in which one or more atoms of a molecule are replaced by an atom or by atoms of a different kind. This type of reaction may be represented by the hypothetical graph

$$\begin{array}{ccccccc} \text{Cu S} & & \text{Y} & & \text{Cu Y} & & \text{S} \\ \bullet-\bullet & + & \bullet & = & \bullet-\bullet & + & \bullet \end{array}$$

This means that the atom of sulphur in the molecule of copper sulphide has been replaced by the hypothetical atom, Y, the sulphur atom assuming all the attributes of pure sulphur. It must be apparent that the new substance, $\begin{array}{c} \text{Cu Y} \\ \bullet-\bullet \end{array}$, may possess essentially different attributes from those which gave to $\begin{array}{c} \text{Cu S} \\ \bullet-\bullet \end{array}$ its homogeneity. This type of reaction will be developed in a subsequent chapter.

*Recent studies in radio-activity seem to indicate that the atom is divisible. M. and Mme. Currie, the discoverers of radium, explain its remarkable illuminating power by the theory that from even a very small quantity of it, parts of its atoms are thrown off continuously, and with inconceivable velocity.

10. Physical and Chemical Changes Compared.—We now have data upon which to base a more scientific distinction between a physical and a chemical change.

1. With a compound substance, the theoretical limit of mechanical subdivision is the molecule of the compound, since it is the molecule which gives to it a chemical individuality. Thus, in copper sulphide, $\overset{\text{Cu S}}{\bullet-\bullet}$, the substance will retain its homogeneity so long as the molecule is not divided. When the molecule is divided, the change is chemical. This may be illustrated by the graph, $\overset{\text{Cu S}}{\bullet-\bullet} = \overset{\text{Cu S}}{\bullet} \bullet$.

2. With a simple substance, the theoretical limit of mechanical subdivision is the molecule composed of atoms of the same kind, for atoms do not, as a rule, exist in the free state. So soon as an atom is freed from combination, it at once unites with another atom or with other atoms. Thus two atoms of sulphur combine and form a molecule of sulphur, $\overset{\text{S S}}{\bullet-\bullet}$. Such a substance is called an element. There can be no *fundamental* chemical change in a simple substance so long as the process is purely analytical.

EXERCISES

Consider the following questions without attempting to give detailed explanations.

1. Is ice a mechanical or a chemical product of water?
2. When milk sours, is the change chemical or mechanical?
3. Is the rotting of wood physical or chemical?
4. What does the rusting of a stove signify?
5. Is steam a chemical or a mechanical product of water?
6. Is sea water a homogeneous substance? Is flour?

CHAPTER II

THE ESSENTIAL PROPERTIES OF SIMPLE AND COMPOUND GASES

HYDROGEN, OXYGEN, HYDROGEN SULPHIDE, CARBON DIOXIDE

11. Properties of Atoms.—Since the atomic theory accepts different varieties of atoms as the ultimate units out of which all ponderable material is constructed, it must give to them all of the essential properties of matter, i.e., indestructibility, extension, impenetrability, weight, etc. Dalton devoted much time to determining the relative weights of the different kinds of atoms, which he designated their “atomic weights.”* He also speculated upon their form and size. It will be the purpose in this chapter to study somewhat in detail a few chemical individuals, in order to obtain data upon which to interpret the essential properties of atoms.

EXPERIMENT 6. *Caution! In the early part of this experiment keep the apparatus away from flame.* Select a 200 cc. flask A (Fig. 4), which is provided with a close-fitting cork or rubber stopper with two perforations. Fit into one perfora-

* Dalton's notion of the composition of substances was probably influenced by the researches of Lavoisier and Proust. Lavoisier, between 1770 and 1780, showed that matter is indestructible, but he made no attempt to explain fully the changes which matter undergoes. Thus he accurately weighed a jar containing a small candle and air, ignited the candle, quickly closed and sealed the jar, and let the candle burn up. On re-weighing the unopened jar, he found that the total weight was unchanged. From such experiments he concluded that matter cannot be destroyed.

Proust, between 1799 and 1807, advocated the view that a given compound always has a constant composition; and that when two elements unite to form more than one compound, the combining proportions increase by *leaps*, and not *gradually*. Thus, he showed that iron and sulphur form two compounds, one of which contains 36.3 per cent of sulphur and the other 53.3 per cent, i.e., there is no *gradual* increase in the per cent of sulphur. He did not, however, explain why the combining proportions show no gradual change. Dalton brought forward his theory of atoms to explain the work of Lavoisier and Proust.

tion a piece of glass tubing B bent at right angles, as in the figure, each arm of which is about 5 cm. long, allowing it to terminate at the under surface of the stopper; through the other perforation pass the stem of a 50 cc. separatory funnel or a thistle tube. The glass cylinder F should have about 400 cc. capacity. Fill it completely with water, and cover its mouth with a glass plate so that no air remains; this may be accomplished by sliding the plate from the side of the opening until it is completely covered. Invert the cylinder over a pneumatic trough, D, letting the

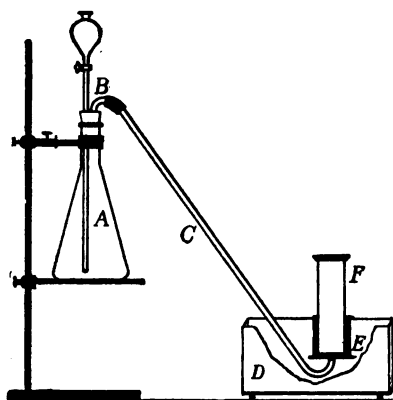


FIGURE 4

pneumatic trough, D, letting the mouth of the cylinder with its glass plate rest upon the perforated stage E, the mouth of the cylinder being below the surface of the water. Place 15 gm. of finely divided zinc in the flask A, and add 50 cc. of dilute sulphuric acid (1:3), and chemical action resulting in the generation of gas will take place. Stopper the flask as shown in the

cut, but do not connect the delivery tube C with F until the chemical action has continued for at least five minutes. If the gas does not come off very briskly upon adding the dilute acid, support the generating flask on a gauze, and apply a gentle heat. The generating flask was filled with air, which must be completely expelled by the escaping gas before the mouth of the tube C is connected with F, otherwise some air will be carried over with the gas into F. *The mixture of air and this gas is very explosive if ignited.* After the air is all expelled from A, insert the end of the delivery tube into the mouth of the receiver F, and collect the escaping gas until it completely

expels the water from the cylinder. Cover the mouth of the cylinder while still under water and remove it to the table, keeping it inverted, and taking care to keep the plate firmly in position to prevent any gas from escaping. Collect three cylinders full of the gas.

12. Properties of Hydrogen.*—Now let us select five attributes—color, odor, solubility in water, combustibility, and power to support combustion, by which this gas may be identified. The color and odor are easily determined. The fact that the gas displaced the water in the receiver is sufficient evidence that it is not readily soluble. Its combustibility may be ascertained by connecting a piece of close-fitting glass tubing D with B (Fig. 5) and applying a lighted match to the glass point E while the gas is being briskly evolved in the generating flask A. Great care should be taken never

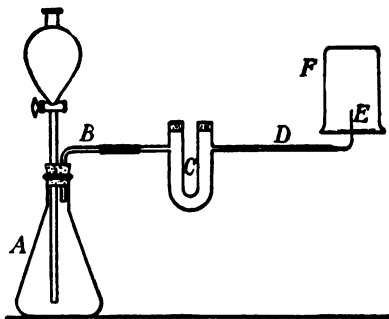


FIGURE 5

to light this gas until energetic chemical action in A has continued for at least five minutes, otherwise the attempt might result in a

*Before the middle of the sixteenth century, the fact that an element or a compound possesses specific properties which distinguish it from all other substances was not recognized. It was *supposed* that the properties (attributes) of salt, mercury, lead, sulphur, etc., are variable, and that in consequence the common metals, e.g., mercury, can be "transmuted" into gold. The agent which was supposed to change the common metals into gold was known as the "Philosopher's Stone." For preparing the philosopher's stone, all sorts of common earths were used. To these, was added a mysterious substance called "Materia prima," which was supposed to give to the mixture of earths, very remarkable powers. The mixture (philosopher's stone) was believed to have power to change many times its weight of base metal, e.g., mercury, into gold. It was also believed that health and life are to be preserved by it. The origin of the belief in this remarkable substance is lost in antiquity. The Egyptians believed in it, and from Alexandria the belief was brought by students of medicine into Western Europe. It dominated completely the scientific thought of the Middle Ages. Van Helmont (1577-1644) first showed that hydrogen and other gases possess *specific* properties.

dangerous explosion. Hold the flame within the mouth of a clean, dry, inverted beaker, and note the moisture which condenses upon its inner surface. The inability of this gas to support combustion may be conveniently shown by igniting a pine splint 15–20 cm. long, holding the cylinder of gas mouth down, and instantly plunging the lighted splint upward into the cylinder as shown in Fig. 6. If the gas is free from air, it will burn quietly at the mouth of the cylinder, but the burning splint will be extinguished.

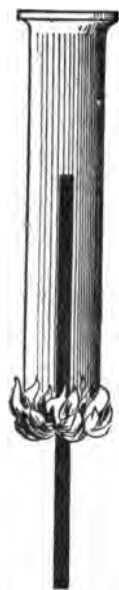


FIGURE 6

In Experiment 6, gas was obtained which was colorless, odorless,* nearly insoluble in water, combustible, but a non-supporter of combustion. Chemists have never succeeded in subdividing this gas into parts which possess attributes other than those described. It is therefore said to be a simple substance, or an element, and is called hydrogen. It was first prepared in a comparatively pure state by the English chemist Cavendish, in 1766. In 1781, Lavoisier observed that when it burns in the air (as in Experiment 6) it produces a watery vapor; so he called it *hydrogen* ("water producing"). It exists free in nature among the gaseous products of most volcanoes, and is found combined with other elements in a very great variety of substances, e.g., water, coal gas, meats, starch, sugar, coal-oil, petroleum, paper, wax, paraffin, etc. It is the lightest known substance, being only .069 as heavy as air. Its lightness may be shown by a simple experiment.

EXPERIMENT 7. Fill the cylinder B (Fig. 7) with hydrogen as directed in Experiment 6, incline it at an angle of about 30° to A, which contains air, remove the plate from B, hold the cylinders in this position for half a minute, close A with a

*The gas prepared from commercial zinc usually has a pronounced odor, because of impurities.

glass plate, invert it, and, having removed the cover, quickly drop a lighted match into it. A more or less violent explosion shows the presence of hydrogen in the upper cylinder.

Hydrogen was formerly used to inflate collodion or rubber balloons; at present, illuminating gas is used because it is much cheaper and fairly suitable.

EXPERIMENT 8. Repeat, with the same precautions, the process described in Experiment 6, substituting iron wire for zinc, and dilute muriatic acid (1:5) for sulphuric acid. Collect and test the gas in the same manner. Is the gas hydrogen? How do you know? How can any substance be identified?

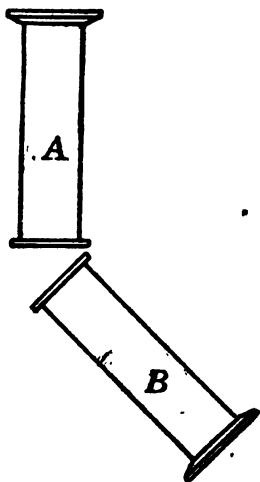


FIGURE 7

13. Some Acids Contain Hydrogen.—Experiments 6 and 8 are very suggestive. In 6, we obtained hydrogen, which is an element, from zinc and sulphuric acid. Since we cannot create matter, it follows that it came either from the zinc or the sulphuric acid. Now zinc is an element; therefore the sulphuric acid must have been the source from which the hydrogen was obtained. This acid is, therefore, a compound substance the molecule of which contains hydrogen. Its molecule may be expressed by the graph, HR , in which R is an unknown atom or combination of atoms.

In Experiment 8, iron, which is an element, and muriatic (also called hydrochloric) acid yielded hydrogen; it follows that this acid is a compound substance whose molecules contain hydrogen. This may be expressed by the graph, HR , in which R is an unknown atom or atoms, but unlike those in sulphuric acid. These experiments teach us that at least two

of the common acids contain hydrogen in combination, and that it may be freed from that combination by using some metal such as iron or zinc.

14. Preparation of Oxygen.—**EXPERIMENT 9.** Make use of the apparatus described in Experiment 6 (Fig. 4). Place 10 gm. of potassium chlorate in a clean, dry mortar, add approximately the same quantity of black oxide of manganese* (manganese dioxide), and grind gently until the two substances are thoroughly mixed. Put the mixture into the flask A, stopper, and heat gently with a small flame until a steady stream of gas is evolved. This may be ascertained by thrusting the end of the delivery tube C under water. Hold a glowing match to the escaping gas. If the match flames up, the gas is relatively pure. Now collect two or three cylinders full.

15. Properties of Oxygen.—For identifying the gas, we may use the attributes selected for hydrogen, i.e., color, odor, solubility in water, combustibility, and power to support combustion. If the experiment is successful, the gas will be found to be colorless, odorless, comparatively insoluble in water, non-combustible, but a vigorous supporter of combustion. The last-named property may be clearly shown by lowering into the gas a match or splint which glows but does not flame. It will instantly flame up with great brilliancy. The flame, however, is not communicated to the gaseous contents of the cylinder. In what way do these attributes differ from those of hydrogen?

Priestley, in England, first prepared this gas in a relatively pure state in 1774 and called it *oxygen*. Since that time it has been studied by many chemists, but no one has succeeded in

*The manganese dioxide used in preparing oxygen should be placed in an iron or porcelain crucible, and heated in a strong gas flame before it is mixed with the potassium chlorate. This will remove any charcoal which it may contain.

subdividing it into parts which possess attributes other than those already described; it is therefore regarded as an element.

16. Occurrence of Oxygen.—Oxygen is the most widely distributed of all the elements. It forms by weight nearly one-half of the earth's crust, eight-ninths of the water, and about one-fifth of our atmosphere. It exists in a free state in the air, and in a combined condition in rocks, starch, sugar, meat, fruits, wood, water, etc. It plays an important role in our lives and must be regularly and abundantly supplied to all living animal tissues to enable them to maintain life.

17. Preparation of Hydrogen Sulphide.—EXPERIMENT 10. *Caution! Perform this experiment under the hood, and do not inhale the gas.* Use the apparatus employed in Experiment 6 (p. 23). Powder coarsely about 20 gm. of iron sulphide, put it into the flask A, add about 50 cc. of dilute sulphuric acid (1:5), connect the apparatus in the usual manner, and heat the flask very gently. When there is a vigorous flow of gas (to be ascertained by thrusting the mouth of the delivery tube C under the water for a moment), collect two or three cylinders full of the gas as directed in Experiment 6.

18. Composition of Hydrogen Sulphide.—Note the color, odor, and solubility in water as directed in Experiment 6; also ignite the gas from a glass jet as there described, and hold the flame in an inverted dry beaker or flask, as shown in Fig. 5. Moisture will be deposited on the sides of the vessel. What does this suggest as to the composition of the gas? Note the odor in the beaker. It is that of an ignited sulphur match. What does this signify? The fact that water was deposited proves that the gas contains hydrogen (compare Experiment 6), and the odor of burning sulphur indicates that it contains sulphur. That these two elements are chem-

ically combined is proved by the fact that the evolving gas does not possess the attributes of either element. It must contain at least both sulphur and hydrogen, and it may contain other elements. Our knowledge of it at this stage may be expressed by the graph, HS. It is called *hydrogen sulphide*, or *sulphuretted hydrogen*.

19. Properties of Hydrogen Sulphide.—If Experiment 10 was successful, the gas is found to be colorless, of a nauseating odor, combustible, but not a supporter of combustion. These attributes will serve to distinguish it from hydrogen and oxygen.

20. Occurrence of Hydrogen Sulphide.—It occurs in nature among the gases issuing from most volcanoes, and in solution in the so-called sulphur waters which are obtained from wells and springs in many parts of America and Europe. The Blue Lick, White Sulphur, French Lick, and Sharon waters are examples. It is a constant product of the decomposition of animal and vegetable substances which contain sulphur in combination. The odor of rotten eggs is due largely to its presence. Inhaled in large quantities, it produces vertigo, lethargy, and nausea. For this reason experiments which call for the use of this gas should be performed under the hood.

21. Preparation and Properties of Carbon Dioxide.—**EXPERIMENT 11.** Use the apparatus described in Experiment 6. Place from 20 to 30 gm. of coarsely powdered marble or limestone in flask A, Fig. 4, and add 50 to 100 cc. of dilute muriatic acid (1: 10), 5 to 10 cc. at a time, from a separatory funnel. A gas will be generated, and when a vigorous flow is secured, collect two or three cylinders full of it. Note its color, odor, and solubility in water, as described in Experiment 6.

Lower a burning splint into a cylinder of it. All flame will be instantly extinguished, showing that it does not support combustion, and that it is not combustible. These attributes serve to distinguish this gas from hydrogen, oxygen, and hydrogen sulphide. It is called *carbonic acid gas*, or *carbon dioxide*. Some insight into its composition may be obtained by preparing it synthetically. This process requires two steps: (1) the preparation of carbon; (2) the combustion of carbon in oxygen.

22. Preparation of Relatively Pure Carbon.—**EXPERIMENT 12.** Place 10 pieces of soft pine, each 2 or 3 cm. long, in an iron crucible, and cover the wood completely with ordinary sand, to partially exclude the air. Support the crucible on a strong wire triangle and ring-stand, and heat it in a blast-lamp flame for 20 or 30 minutes. Allow the crucible to cool, and pour off the sand. The wood will have been completely charred and the product is black and brittle. Place one or two of the pieces in a mortar and reduce to a fine powder. If the crucible was heated sufficiently, this will be done easily. Remove some of the powder to a sheet of clean white paper, and examine it with a lens to see whether it is homogeneous. If so, it must be a chemical individual.

23. Properties of Carbon.—Test the color, odor, and solubility of the powder in the usual manner. The combustibility may be shown by placing some of the powder in a deflagrating spoon, A, Fig. 8, heating it to redness in a blast-lamp flame, and quickly plunging it into a cylinder of pure oxygen B, keeping the mouth of the cylinder protected from the outside air by a piece of paper, as shown in the figure. If the experiment is successful, the contents of the spoon will

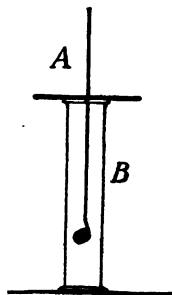


FIGURE 8

glow. This black, odorless, and combustible substance is *carbon*. When perfectly pure, it has never been subdivided into parts which possess attributes different from those here enumerated. It is therefore an element, and one of the most abundant, and most widely distributed. It occurs in nature both free and combined.

24. Varieties of Carbon.—Carbon is found in the free state in three distinct forms: diamond, graphite, and coal or amorphous carbon.

(1). The *diamond*, which represents the purest form of carbon, is found in India, Brazil, and especially at Kimberley, South Africa, where the largest diamond mines in the world occur. It is one of the hardest of all known substances,* and is cut only with its own powder. It possesses great brilliancy, the property to which it owes its value as a gem. If heated to a very high temperature without air, it swells up perceptibly, and finally crumbles into a black, more or less amorphous mass, without loss in weight. It burns at a high temperature in an atmosphere of oxygen, yielding as its sole product carbon dioxide.

(2). *Graphite* (also called black lead, plumbago, etc.), another form of carbon, is a grayish-black solid with a metallic luster. It feels greasy to the touch, and is a good conductor of electricity. It is mined in England, Siberia, New York, Vermont, and elsewhere. It is combustible only with great difficulty. For this reason, and because of its luster, it is made the chief ingredient in stove polish, and other polishes for iron. It is sometimes used as a lubricator to diminish the friction of belts and other parts of machinery. It leaves a leaden-gray mark on paper, and is therefore extensively used in the manufacture of "lead" pencils. In the manufacture of coal-gas, a very hard coating is formed on the retorts which has been

* Some varieties of boron are harder.

called gas-carbon, and is generally regarded as a variety of graphite. It is used for making the carbon points for the arc electric light.

(3). *Amorphous carbon* is so-called because its particles do not possess crystalline structure. The most common *natural* form of this variety is coal. Charcoal and coke are *manufactured* varieties of amorphous carbon.

25. Preparation and Uses of Amorphous Carbon.—

All varieties of wood contain at least three elements in combination—carbon, hydrogen, and oxygen. When wood is heated to the kindling point with free access of air, its characteristic molecule is broken up. The hydrogen and oxygen combine to form water, and the carbon combines with the oxygen to form carbon dioxide. Both of these products of combustion are gaseous compounds which are dissipated into the surrounding atmosphere, leaving only a small quantity of ash. But if the wood is heated to the kindling point while the air is partly excluded, the hydrogen combines with the oxygen to form water, and the carbon remains as a non-volatile, black, amorphous mass. This is charcoal. The actual chemical changes are more complicated than those mentioned, but they are the essentials. Amorphous carbon may be prepared by heating *any* animal or vegetable tissue to a high temperature, if the free access of air is prevented. This may be shown by placing a piece of any such tissue, e.g., wool, wood, sugar, starch, silk, fat, albumen, or cotton in a crucible, covering it with sand to exclude the air, and heating to dull redness. In baking, broiling, or frying food, care is taken to avoid excessive temperatures. Otherwise the above described decomposition occurs on a small scale, with the separation of more or less carbon. When such changes take place, the food is said to have been scorched or “burned.”

If ordinary soft coal is placed in brick ovens, each of which

has a small opening at the top, and then ignited and allowed to burn with only a very small supply of air, a variety of amorphous carbon called "coke" is produced. Coke is extensively used in blast and other furnaces, because it produces a much more intense heat than ordinary coal.

Carbon occurs in combination with other elements in a great variety of substances. It is a constituent of every living thing, and, in combination with hydrogen, forms the various mineral oils, such as petroleum and asphaltum. When one of these is incompletely burned, amorphous carbon separates. When, for instance, the flame of an ordinary kerosene lamp or candle is insufficiently supplied with air, it "smokes." This variety of amorphous carbon is known commercially as "lampblack," and is used extensively in the preparation of printer's ink, "lampblack" paint, etc. By heating bones in the absence of air, we get another variety of charcoal called "boneblack," which contains only a small proportion of carbon; but the carbon is so distributed through the porous mineral matter of the bone as to make it quite effective. Blood mixed with sodium carbonate and charred is commonly called "animal charcoal." Amorphous carbon obtained from wood or animal tissue possesses some exceptional and useful properties. Some of these may be easily shown.

EXPERIMENT 13. Put about 5 gm. of pulverized charcoal into a cylinder or other suitable vessel, add 5 or 10 cc. of an indigo, cochineal, litmus, or turmeric solution, shake vigorously for a moment (add a little water if necessary), and then filter through a small, moist filter. The solution will be colorless. In sugar refineries, this property of charcoal is taken advantage of to transform the raw brown sugar into the white varieties.

EXPERIMENT 14. Place from 10 to 20 gm. of charcoal or boneblack in a flask, add 15 or 20 cc. of water, through which hydrogen sulphide has been allowed to bubble slowly, cork securely, shake for fifteen or twenty minutes, filter, and compare

the odor of the filtrate with that of the original fluid. Because of its power to decolorize and deodorize liquids, charcoal is useful in water filters. Water stored up in reservoirs contains dust, dissolved organic products, and often disagreeable gases which result from the putrefaction of the organic matter. Filtering such water through a sufficient quantity of charcoal removes these objectionable constituents.

26. The Combustion of Carbon in Oxygen.—EXPERIMENT 15. The apparatus shown in Fig. 9 will be found convenient for the synthesis of carbon dioxide. A is a receiver

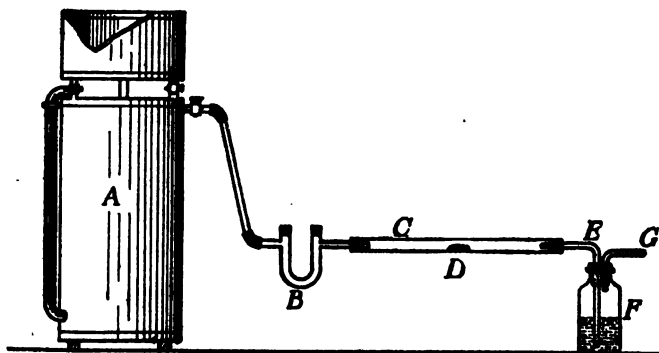


FIGURE 9

of oxygen; B is a tube filled with calcium chloride for drying the oxygen as it passes into C; C is a tube of hard glass about 30 cm. long and 1 cm. in diameter, provided with well-fitting stoppers with single perforations; F is an ordinary wide-mouthed bottle or flask provided with a stopper with two perforations. The glass tube E which connects C with F should extend nearly to the bottom of the bottle. Fill the bottle two-thirds full of lime water,* put about 2 gm. of the pulverized carbon (prepared in Experiment 12) in the tube C at D,

*This should be prepared as follows: Pulverize about 5 grams of unslaked lime, add about 200 cc. of water, stir vigorously for from five to ten minutes, and filter.

connect the apparatus as shown in the cut, heat the tube at D to dull redness, turn on a slow stream of oxygen from A, and allow it to flow until the carbon at D is completely consumed. It is apparent that a chemical union has taken place, since the carbon (which is not volatile at such a temperature) has disappeared.

Coincident with the disappearance of the carbon, a white precipitate will form in F. This is due to the action of the burned carbon (carbon dioxide) on the lime water. This precipitate makes clear the purpose of the experiment, namely, to fix the product of the combustion, and thus prevent its escape into the air through the safety tube G. When the combustion of the carbon is complete, stop the process, filter off the liquid from the precipitate in F, put the filter paper with its precipitate into the bottle F, add 5 to 10 cc. of dilute sulphuric acid, and test the escaping gas for the attributes of carbon dioxide as in Experiment 11.

27. Carbon in Carbon Dioxide.—The presence of carbon in the carbon dioxide molecule may be shown analytically.

EXPERIMENT 16. *Caution! In this experiment be very careful not to touch the potassium with the bare fingers. Always grasp it with pincers or with paper held in the fingers. It ignites spontaneously when it touches moisture, and may produce deep and painful wounds.* A, Fig. 10, represents the generating flask used in Experiment 6; C is a tube of hard glass about 30 cm. long and 1 to 1.5 cm. in diameter; B is a U-tube about 15 cm. long and 10 cm. wide, filled with fused calcium chloride. The contents of the tube should be held in place by plugs of ordinary cotton before inserting the stoppers. Dry a piece of metallic potassium by pressing it carefully between pieces of dry filter paper; put it into the tube C at D, and connect the apparatus as shown in the cut. Generate a vigorous flow of carbonic acid gas in flask A, from limestone

and dilute muriatic acid (Experiment 11), and heat the tube C at D until the lump of potassium melts to a silvery bead. It will be quickly coated with a deposit of finely divided carbon. Allow the tube C to cool, disconnect it and put it into a vessel of water with sufficient depth to cover the potassium at D. Let it stand until the bead softens and is released from the tube. Filter off the liquid, dry the solid on the filter paper, and examine it for carbon as directed in Experiments 13 and 14.

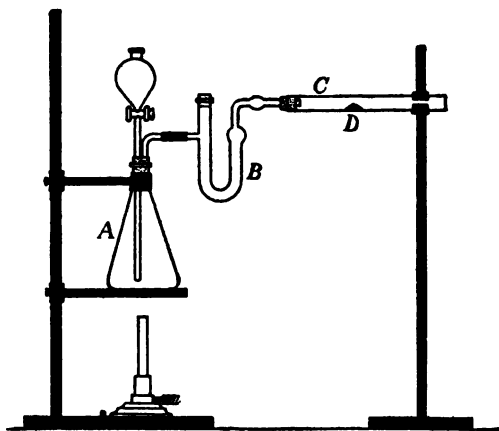


FIGURE 10

The interpretation of this experiment is comparatively simple. Potassium is an element. The tube C contained only this element and the compound gas, carbon dioxide; the carbon must therefore have been set free from the latter.

28. Composition of Carbon Dioxide.—It follows from Experiments 15 and 16 that this gas is a compound of carbon and oxygen. Our knowledge of the structure of its molecule may be represented by the graph, CO. It may be that more than one atom of oxygen is combined with each atom of carbon, but at this point our experimental data are not adequate to answer this question. (There are, in fact, two atoms of oxygen, giving the formula CO_2 .)

29. The Physical Properties of Gases.—We are now acquainted with four gases, two of which, oxygen and hydrogen,

are elements; and two, hydrogen sulphide and carbon dioxide, are compounds. These gases possess the essential attributes of all true gases. Accepting them as representative, we shall use them to study the general physical properties of gases.

(1). *All gases have weight.*—This is one of the essential properties of matter, and needs no experimental demonstration.

(2). *Some are heavier than others.*—The relative weight of carbon dioxide and air may be illustrated by pouring the former from one cylinder, into a second cylinder which contains a lighted candle. The candle flame will be quickly extinguished. This shows that the carbon dioxide is heavier than the air, and may be poured from vessel to vessel, somewhat like a liquid.

(3.) *All gases diffuse.*—The power of a gas to diffuse through inconceivably small openings may be illustrated by the following experiment:

EXPERIMENT 17. B, Fig. 11, is an unglazed, porous cup about 15 cm. long and 4 cm. in diameter, which is made with a flange or shoulder C about 1 cm. wide. Fit into this cup an india-rubber stopper with one perforation, insert a glass tube 100 cm. long which securely fits the perforation in the stopper, dip the lower end of the tube into



FIGURE 11

a flask of water, and quickly lower upon the cup B a cylinder A, which is filled with hydrogen. Bubbles will soon be observed to come from the water in E. The reason is that

the hydrogen in A diffuses faster into B than the air in B can diffuse into A. This results in increased pressure in B, which expels some of the air through E.

(4.) *Limit of diffusion.*

EXPERIMENT 18. Select two cylinders, A and B (Fig. 12), of like diameter and capacity, whose edges are well ground and well fitting, and render them air-tight by greasing the ground surfaces with lard or vaseline. Completely fill A with pure hydrogen (see Experiment 6), and B with carbon dioxide. It has been pointed out (p. 27) that hydrogen tends to rise and carbon dioxide to fall (p. 38) in air, because the one is much lighter and the other much heavier than the air. Now invert the cylinder of hydrogen over that containing carbon dioxide as shown in the cut, remove the intercepting glass plates, adjust the greased edges of the openings so that no gas can escape, and let the cylinders remain in this position for twelve hours. Re-insert the glass plates between them, taking great care not to allow the ingress of air or egress of gas, and invert each over a strong solution

of caustic soda (50 gm. of sodium hydroxide dissolved in 500 cc. water), so that the mouth of each cylinder is well immersed in the liquid. Remove the glass plates and let them stand over night. The liquid will be observed to have risen in each cylinder to a like height. Caustic soda dissolves carbon dioxide very rapidly, while it has no effect on hydrogen. The fact that the liquid rises to the same height in each cylinder, therefore shows that each contained the same quantity of the two gases. This experiment also tends to confirm the assumption made on page 17, that the musk which was converted into gas by evaporation diffused uniformly throughout the air of

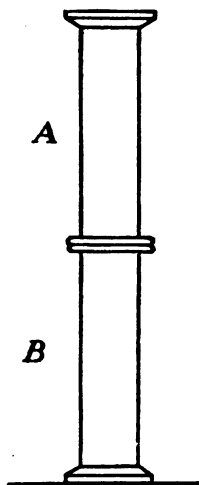


FIGURE 12

the inclosed space. Test the residual gas in each cylinder for hydrogen. Here we have a heavy gas diffusing upward, and a light one downward, until the two are uniformly mixed. This phenomenon illustrates the law of diffusion for all gases: *Two communicating gases in different vessels continue to diffuse until both vessels contain an identical mixture of the two.*

(5.) *All gases are compressible.*—By compressibility is meant the property of matter by virtue of which a given volume becomes smaller under increased pressure. The volume of any gas decreases when the pressure upon it is increased, because the gaseous molecules are brought closer together.

30. Relation of Pressure to Volume.—A fact of no less importance is the ratio of pressure to the volume. It can be shown that the volume of a gas varies *inversely* as the pressure upon it; that is, the product of the pressure, P , and the volume, V , is a constant, C . This relation is usually expressed by the equation, $P \times V = C$. In other words, if the volume of a gas at a given temperature and under one atmosphere pressure is 10 cc., the volume will be 5 cc. when the pressure is increased to two atmospheres, and 20 cc. when the pressure is reduced to that of one-half atmosphere. The statement of the relation between the volume of a gas and the pressure to which it is subject, is known as *Boyle's law*.

31. Mass and Density.—It is apparent that when a given volume of gas is subjected to increased pressure, the quantity (mass) of gas is not altered, but only crowded into a smaller space. If an initial volume of gas under a given pressure weighs .001 gm., it will still weigh .001 gm. under increased or decreased pressure. Under varying pressures, therefore, the mass of a gas is independent of its volume. The mass of a gas (or other substance) is measured by the earth-pull, which we call *weight*. Thus a sphere of lead and of cork each weigh-

ing one pound are said to have the same mass, because the earth-pull on each is the same. They have, however, very unequal volumes. When the volumes of cork and lead are equal, their respective weights (masses) are unequal. One is therefore said to be more *dense* than the other. That property of matter by virtue of which either equal volumes contain unequal masses, or unequal volumes contain equal masses, is called *density*.

EXAMPLE. One cc. of water weighs 1 gm., and 1 cc. of mercury weighs 13.6 gm. Mercury therefore has a density 13.6 times that of water. One cc. of water transformed into vapor would occupy many times that volume, but its mass would remain unchanged. The density of a substance, therefore, depends upon its *mass and volume*. The mass remaining the same, density is *inversely* proportional to volume; the volume remaining the same, density is *directly* proportional to mass. The relation is usually expressed by the ratio:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}, \text{ or } D = \frac{M}{V}$$

32. Relation of Volume and Temperature.—It is well known that gases expand when heated and contract when cooled. Physicists have shown that all true gases expand equally for equal rise of temperature. It is found that for each degree of increase of temperature, a gas, measured originally at 0°, will expand about $\frac{1}{273}$ of its volume. Thus 273 volumes of hydrogen at 0° become 274 volumes at 1°, 275 volumes at 2°, 276 volumes at 3°, 272 volumes at -1°, and 270 volumes at -3°. This gives a basis for determining the volume of a gas at different temperatures.

1. What would be the volume of 1000 cc. of hydrogen measured at 0°, after being heated to 25°?

We would have, $273 : 273 + 25 :: 1000 : X$;

$$X = \frac{1000 \times 298}{273}$$

2. What would be the volume of 1000 cc. of hydrogen measured at 25° after being cooled to 0° ?

The following proportion would obtain:

$$273 + 25 : 273 :: 1000 : X;$$

$$X = \frac{273 \times 1000}{298}$$

3. What would be the volume of 1000 cc. of hydrogen measured at 25° , after being cooled to 20° ?

$$273 + 25 : 273 + 20 :: 1000 : X;$$

$$X = \frac{1000 \times 293}{298}$$

The combined influence of temperature and pressure upon the volume of a gas may be stated thus: *The volume of any true gas varies directly as the temperature, and inversely as the pressure.*

Summary.—In the preceding pages we have discovered:

1. That a chemical change is the union or separation of two or more atoms.
2. That an element is a substance which has never been subdivided into parts which possess essentially different attributes.
3. That hydrogen, oxygen, iron, zinc, sodium, and carbon are elements.
4. That hydrochloric and sulphuric acid are compounds (not elements), and that each contains combined hydrogen.
5. That carbon dioxide and hydrogen sulphide are compound gases.
6. That the molecule of carbon dioxide contains carbon and oxygen, in proportions which were not determined.
7. That the molecule of hydrogen sulphide contains hydrogen and sulphur, in proportions which were not determined.

8. That atoms, though inconceivably small, possess all the general properties of matter.

9. That gases are compressible, and possess the power of diffusion.

10. That the volume of all true gases increases with increase of temperature, and decreases with increase of pressure.

EXERCISES

1. How does Experiment 6 show the lightness of hydrogen?
2. Since muriatic and sulphuric acid both contain hydrogen, why are they not identical?
3. How does the separation of sulphur in Experiment 10 show that hydrogen sulphide is a compound gas?
4. How does Experiment 14 explain the deodorizing power of charcoal?
5. Prove that fat contains carbon.
6. Why is a candle burning in a jar or a bottle quickly extinguished?
7. What would be the effect upon animal life, if gases did not diffuse?
8. Would a balloon filled with hydrogen float in a vacuum?
9. Calculate the volume of 33 cc. of hydrogen measured at 750 mm. of pressure, when the pressure falls to 700 mm., temperature being constant.
10. Could hydrogen and oxygen be brought to the same density? If so, how? If not, why not?
11. What would be the volume of 15 cc. of carbon dioxide measured at 24° , after being cooled to 13° ?
12. What would be the volume of 1000 cc. of hydrogen measured at 0° , when cooled to -273° ?
13. What is the pressure per square inch on the walls of a vessel which contains 1000 cc. of oxygen under three atmospheres pressure?
14. What will be the volume of the oxygen mentioned in 13, when the pressure is reduced to one atmosphere?

CHAPTER III

THE DETERMINATION OF ATOMIC MASS

It is the purpose of this chapter to show how the relative mass of atoms, commonly called their atomic weight, may be determined. A few preliminary experiments are necessary to interpret the results.

EXPERIMENT 19. *Caution! Keep all flames away from the hydrogen generator.*

Have ready a jar of oxygen. Generate pure dry hydrogen, using the apparatus outlined in Fig. 5, p. 25. To ascertain when the hydrogen is pure, collect a test-tube full over water, carry it at least four feet from the generator, and ignite. When pure, the hydrogen will burn quietly. It is then safe to ignite the jet at E. Fit over the jet a piece of pasteboard large enough to cover the jar F, and introduce the burning hydrogen into the jar of oxygen, F. Since F contains only hydrogen and oxygen, the flame means a chemical union of these elements. The product of this union is the water which appears in tiny drops on the sides of the receiver. This means that a molecule of water contains hydrogen and oxygen in combination. The atomic theory declares that the molecule must be made of at least one atom of each. Our present knowledge of this molecule may be expressed by the graph HO , but whether the atoms combine in this proportion will be determined by Experiment 20.

33. The Electrolysis of Water.—A convenient apparatus for determining this proportion is shown in Fig. 13, Experiment 20.

EXPERIMENT 20. Fill the central tube D with water acidulated with from 20 to 30 cc. of dilute sulphuric acid (1 : 10), which, on opening the stopcocks A and B, will rise and fill the gas-collecting tubes AX and BY. Connect the platinum electrodes X and Y with three or four La Clanche or dichromate cells so that the electric current will flow from X toward Y. A stream of minute bubbles will rise from each of the electrodes and collect in the upper portion of the tubes. Allow the action to continue about 20 minutes, break the electric connection, wait until the gas in the lower portion of the tubes rises to the top, read off and record each volume,* and repeat the process five or six times. The proper tests (pages 25, 28) will show the gases to be hydrogen (tube B) and oxygen (tube A). The electric current has in each case separated the water into two volumes of hydrogen and one volume of oxygen. Therefore this is the proportion in which they are combined in water.

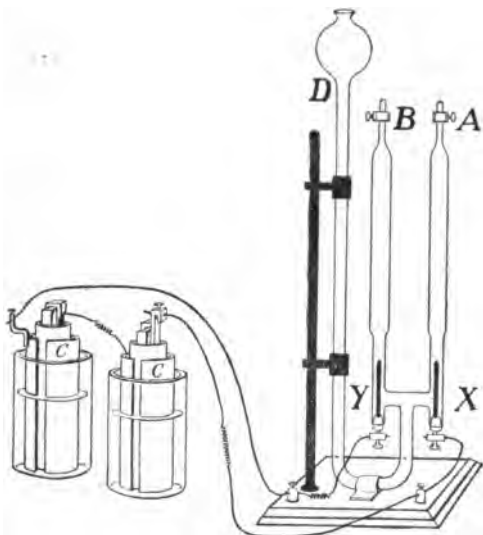


FIGURE 13

* A student obtained the following results:

Tube B	Tube A
10 cc.	4.5 cc.
18 cc.	8.8 cc.
25 cc.	12.4 cc.
35 cc.	17.5 cc.

34. Composition of Water by Volume.—Long ago, Avogadro proved that equal volumes of elementary gases under like conditions of temperature and pressure, contain the *same number of atoms*. If, therefore, the volume of one gas (B) is twice that of another (A), it has twice the number of atoms. It follows that in a molecule of water there are always two atoms of hydrogen combined with one atom of oxygen. This may be expressed by the formula H_2O , the numeral denoting two atoms of hydrogen. When no numeral is used, one atom is always understood. The organization of the molecule of water may be shown by the graph, $\overset{\text{H}}{\bullet} \text{---} \overset{\text{O}}{\bullet} \text{---} \overset{\text{H}}{\bullet}$.

35. Determination of the Atomic Weight of Oxygen.—By determining the proportion by weight in which hydrogen and oxygen combine we can find the relative masses of their atoms.* The process is essentially as follows: Metallic copper, absolutely pure and in the form of a fine powder, is obtained. A small amount of this copper is then weighed accurately, and heated in a stream of oxygen until it becomes dark colored. This change must be synthetic, and is clearly that represented by the graph $\text{Cu} + \text{O} = \text{CuO}$,† i.e., oxygen has united with the copper to form copper oxide. This copper oxide is accurately weighed, and the increase over the weight of the copper, is the weight of the oxygen combined with the copper. This is carefully noted. The purpose up to this point has been to obtain oxygen in a fixed form, and to find the exact weight of the oxygen so fixed.

This weighed copper oxide is next heated in a stream of pure dry hydrogen, Fig. 14. The oxide is reduced to metallic copper, and at the same time water forms ($\text{CuO} + \text{HH} = \text{Cu} + \text{H}_2\text{O}$) and is absorbed in a previously weighed tube of

*The experiment is too difficult for beginners. It should be performed by the teacher, and the results placed before the students for interpretation.

†It should be kept in mind that CuO is only a hypothetical proportion which must be verified or corrected later.

calcium chloride, F. Upon reweighing the tube, it will be found to weigh more. This increase is clearly the weight of the water that has been formed by the combination of the weighed quantity of oxygen with hydrogen, and we now know the exact amount of water that our exact amount of oxygen is capable of forming. Let us suppose that the oxygen (in the copper oxide) weighed .16 gm. and that the amount of water formed weighed .18 gm. All of the oxygen, .16 gm., was combined with hydrogen to form water. It follows that of the 0.18 gm. of water formed, 0.16 gm. by weight was oxygen. The remaining 0.02 gm. must have been hydrogen. Therefore, 0.02 gm. of H combined with 0.16 gm. of O to form 0.18 gm. of H_2O .

I. *Preparation of Copper*.—A, Fig. 14, is a hydrogen generator. B is a bottle containing 50 cc. of concentrated sulphuric

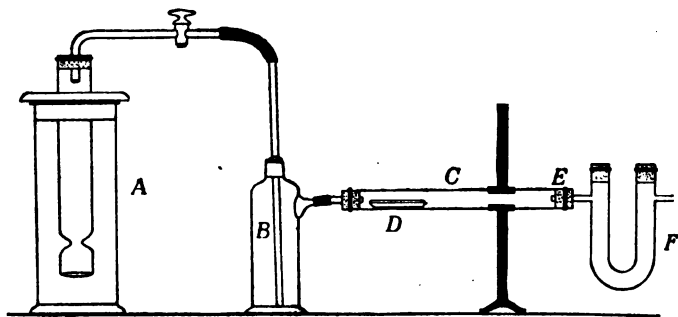


FIGURE 14

acid for drying the gas as it is driven into the tube C. This tube (about 2 cm. in diameter and 30 cm. long) is made of hard glass, and is connected with B by a close-fitting rubber stopper. D is a small porcelain boat.

Fill the boat two-thirds full of pure copper oxide, taking great care that none of it adheres to the edges or outside, place it in the tube C at D, omitting the U-tube F. Connect the apparatus, pass a slow stream of hydrogen (for about ten

minutes) until all air is expelled, and heat that part of the tube which supports the boat as hot as is possible with a bunsen flame, at the same time maintaining the flow of hydrogen. If moisture condenses upon the extremities of the tube, heat these portions until they are perfectly dry. Remove the lamp and allow the tube C to cool thoroughly before removing the boat. While the tube is cooling, a very slow stream of hydrogen should pass through the apparatus. The compound in D should take on a dull red color, and should have all the attri-

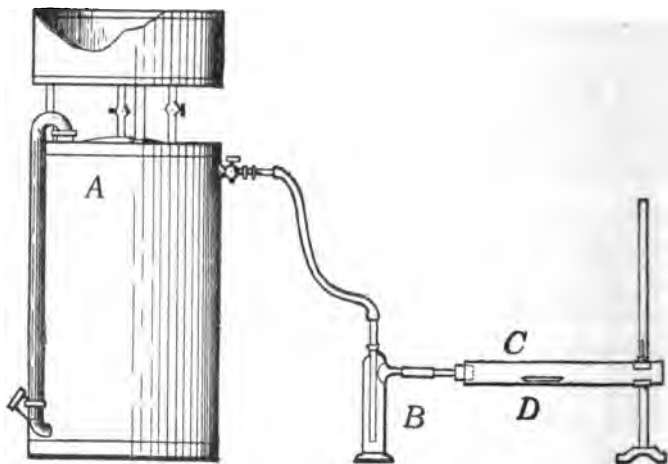


FIGURE 15

butes of copper. Weigh the boat and contents, lifting it with a clean pair of crucible tongs. Suppose the weight of boat and contents = 23.00 gm.

II. *Weight of oxygen in copper oxide.*—Again put the boat with its copper into the tube C, Fig. 15, and allow a slow stream of oxygen to pass through the apparatus for about ten minutes, until all hydrogen is expelled; otherwise there will be danger of a violent explosion on re-heating the tube. Now heat that portion supporting the boat as hot as a bunsen flame will permit,

and keep it hot for at least ten minutes. The contents will take on a dark brown-black color. Remove the flame, place the boat in a desiccator until perfectly cool, then weigh it accurately. If the weight of the boat + copper + oxygen = 23.16 gm., and the weight of boat + copper = 23.00 gm., the weight of oxygen absorbed = 0.16 gm.

III. *Combination of Hydrogen and Oxygen by Weight.*—The tube F, Fig. 14, is filled with fused calcium chloride, which absorbs water with great energy. Weigh the tube F accurately, introduce the boat with its copper oxide into C, and connect the tube F with C by a closely fitting rubber or cork stopper with one perforation. The arm of F should extend only to the inner surface of the stopper. Now pass a slow stream of hydrogen through the apparatus until all air is expelled. This may be ascertained by collecting some of the escaping gas over water and testing its combustibility. If it burns quietly, it is free from air. Then apply a strong heat at D. The contents of the boat will assume slowly the characteristic appearance of pure copper, and at the same time water will collect at the point E. Continue the heat until the contents are uniformly copper-colored. Advance the flame slowly toward E until all moisture is driven into F. Disconnect and weigh the tube F accurately.

Suppose the weight of tube after passing	
hydrogen	= 35.18 gm.
Suppose the weight of tube before passing	
hydrogen	= 35.00 "
	0.18 "

Then 0.18 gm. = weight of water formed by uniting 0.16 gm. of oxygen with hydrogen.

In Experiment 20 it was shown that in the molecule of water two atoms of hydrogen, H_2 , are combined with one atom of oxygen, O. But by weight $H_2 : O :: 2 : 16$.

One atom of oxygen is therefore 8 times as heavy as two atoms of hydrogen, or 16 times as heavy as one. The *absolute* or actual weight of any atom is unknown, but the hydrogen atom is the lightest known. Chemists, therefore, usually take its weight as unity, and express all other atomic weights in multiples of it. The atomic weight of hydrogen therefore = 1, and of oxygen = 16.

The International Committee of Chemists, which adopted a scale of "International Atomic Weights," accepted the atomic weight of oxygen as 16 and expressed all other atomic weights in terms of this standard. Both standards are used, but in most cases it is simpler to express the atomic weight of all other elements in multiples of the hydrogen = 1 standard. This standard will be used in determining the atomic weight of copper.

36. The Atomic Weight of Copper.—The determination of the atomic weight of copper involves the determination of the proportions by weight in which copper and oxygen combine.

EXPERIMENT 21.* Place about 1 gm. of pure copper oxide in a porcelain boat whose weight is known, and heat it in the colorless bunsen flame until it ceases to lose weight.

Suppose weight of boat + copper oxide	= 12.7957 gm.
Suppose weight of boat	= 12.000 "
Weight of copper oxide	= 0.7957 "

Place the boat with its contents in tube C, Fig. 14, p. 47, connect the apparatus as shown in the cut, omitting the tube F; pass a slow stream of hydrogen through the apparatus, and when all air is expelled (see Experiment 6) heat strongly that part

*In most cases this experiment should be performed by the teacher, and the results put before the class for discussion.

of the tube which supports the boat. Maintain the flow of hydrogen and the heat until the contents of the boat assume a uniform copper color. During this process considerable moisture will condense on the walls of C. Move the flame cautiously back and forth until it is completely expelled from the tube. Remove the lamp and let the tube cool while a slow stream of hydrogen passes through it. If the boat were removed from the tube while hot, the copper would immediately absorb oxygen on exposure to the air. Weigh the boat and the copper. Repeat the heating and weighing as above directed until the combined weight of boat and copper ceases to change when re-heated and re-weighed. This is to assure the operator that *all* oxygen has been withdrawn from the copper. The chemical changes may be expressed by the assumed graph, $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$.

Suppose weight of boat + copper = 12.6357 gm.

Suppose weight of boat = 12.000 “

Weight of copper in copper oxide = 0.6357 “

In this case 0.7957 gm. of copper oxide contained .6357 gm. of copper, and .16 gm. of oxygen. This gives the ratio of combination by weight. If the copper and oxygen are combined atom for atom in copper oxide, we have,

$16 : X$ (the atomic weight of Cu) $:: .16 : .6357$

$.16 \times X = 16 \times .6357$

$X = 63.57$, the atomic-weight of copper, *if copper and oxygen are combined atom for atom*. By means which will not be stated here, these are known to be the proportions of Cu and O in copper oxide.

37. Specific Atomic Weights.—These determinations of the atomic weight of copper and oxygen will give the student

some notion of one method by which atomic weights of elements are determined. It would be an ideal plan for the student to determine the atomic weight of each of the elements with which he is immediately concerned. Such a plan is, however, impracticable. We shall, therefore, accept the atomic weights of the important elements as they have been determined by others. Our faith in the results is increased by the fact that different investigators have arrived at practically the same values by diverse methods. The following illustration will suffice to show the striking similarity in the results:

	CLARK	RICHARDS	GERMAN	
Lead	206.92	206.92	206.90	} Atomic weights
Copper	63.60	63.60	63.60	
Iron	56.00	55.90	56.00	
Zinc	65.40	65.40	65.40	

For a complete list of the elements and their atomic weights see Appendix.

EXERCISES

1. How may the direction in which an electric current is flowing be determined?
2. What would be the effect if the current were to pass from Y to X, Fig. 13, Exp. 20?
3. How may chemically pure hydrogen be prepared without the use of zinc or other metals?
4. What is the formula of a compound of hydrogen and oxygen which contains thirty-two parts by weight of oxygen and two parts of hydrogen?
5. A quantity of copper oxide is found to contain 1.271 gm. of copper, and 0.16 gm. of oxygen. Determine its composition.
6. How many gm. of copper are combined in 7.6 gm. of copper oxide?
7. Determine the per cent of oxygen by weight, in 100 gm. of copper oxide.
8. Sixteen gm. of oxygen occupy about 11,000 cc.; how many cc. of it will be required to burn 2 gm. of hydrogen?

9. How many liters of oxygen (23 liters contain 32 gm.) will be required to burn 12 gm. of pure lampblack to carbon dioxide, CO_2 ?

10. A compound of iron and sulphur contains fifty-six parts by weight of iron, and sixty-four parts by weight of sulphur. What is the ratio of the atoms in the molecule?

CHAPTER IV

THE DETERMINATION OF FORMULAS

We shall accept the atomic weights given in the appendix in determining the formulas of some compounds which are very important in the development of our subject. In preparation for these determinations, it will be necessary first to study the attributes of several elements.

CHLORINE, Cl (At. Wt. 35.45)

Chlorine was first isolated and its properties examined by Scheele, a Swedish chemist, in 1774. Its elementary character was shown by Gay-Lussac in France in 1809, and independently by Davy in England in 1810. Because of its extraordinary activity it does not occur free in nature (except as small quantities are given off by active volcanoes), but it is found in combination in common salt, and in many other minerals.

Preparation of Chlorine.—Caution! Perform all experiments with chlorine under the hood. Avoid inhaling the gas.

EXPERIMENT 22. Use the apparatus shown in Fig. 16. A is a 200 cc. flask; E is an ordinary glass cylinder; D is a glass tube about 40 cm. long, which is connected with B by a very short piece of rubber tubing. The tube D should be passed through a thick paper cover F, which serves to prevent the diffusion of gas into the surrounding air. Place the apparatus under the hood, put about 50 gm. of powdered manganese dioxide into the generating flask A, add sufficient water to moisten it thoroughly, connect the apparatus as shown in the cut, add about 50 cc. of the strongest hydrochloric acid from the funnel C, and apply a gentle heat. In a short time the bottom of the

receiving cylinder E will be covered with a yellowish-green gas which will gradually accumulate until it reaches to the covering F. Collect two other cylinders full of it. The first cylinder will contain some air mixed with the gas; the contents of the other two should be practically free from air.

38. Properties of Chlorine.

Chlorine.—The gas is comparatively soluble in water, non-combustible, a very poor supporter of combustion (carbon does not burn in it), has a penetrating pungent odor, producing great irritation of mucous surfaces. It is an element, because it has never been

subdivided into parts which possess attributes at variance with those above enumerated. It is so active that it breaks up many compounds under ordinary conditions. The following studies will serve to illustrate this power.

I. Combustion of Sodium in Chlorine.

EXPERIMENT 23. *Caution! The metallic sodium used in this experiment explodes when brought into contact with water. Do not touch it with the fingers; always use pincers. Keep the face well away from it.*

Cut a thin piece of metallic sodium about 5 mm. square, press it between dry filter papers to remove any naphtha (sodium is always kept in naphtha), heat it in a clean deflagrating spoon until it melts, and plunge it instantly into a receiver of dry chlorine; it will ignite and burn brilliantly with an intensely yellow flame. When combustion ceases, remove the contents

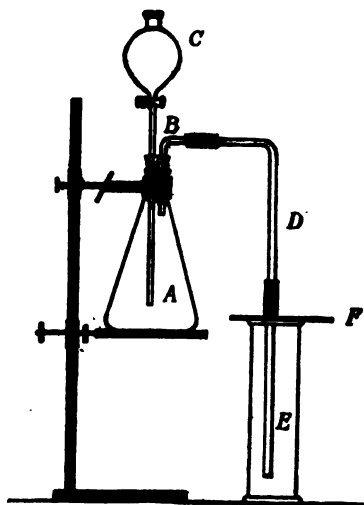
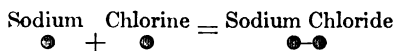


FIGURE 16

of the spoon to a clean glass plate and examine its physical properties. Does it possess the attributes of the original metal? Of chlorine? Is it homogeneous? Taste a little of the powder, having first examined it carefully to make sure that *no metallic sodium remains*. What is it?

Since only two elements were present in the receiver, the action must have been *synthetic*, and the resulting substance must be a compound of these elements. This activity may be expressed by the graph,



Our data, however, do not show that the elements combined in the proportion here assumed.

II. Bleaching Properties of Chlorine.

EXPERIMENT 24. Moisten a piece of highly colored calico, a red rose, a nasturtium, or other highly colored flower, and a strip of newspaper or other printed matter, and lower them into a receiver of chlorine. The calico and the flowers will be bleached, but the printer's ink, which consists chiefly of carbon, will retain its color.

The color in flowers and other vegetable tissue is due to the presence of very complex molecules. The chlorine probably combines with the hydrogen in the moisture, thus liberating oxygen, which breaks up these complex molecules, changing their composition so that the physical attributes, of which color is one, are materially altered. It is this property which gives to chlorine its chief commercial importance.

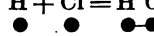
39. Commercial Value of Chlorine.—Before the close of the eighteenth century, commerce depended upon the bleaching action of the atmosphere and the sun's rays to whiten fabrics which were made from vegetable fiber. The cloth was spread out on the grass where direct exposure to the sun's rays was assured, and was sprinkled with water many times a day. After several months of such treatment, the cloth was rendered white. It was observed that certain

districts in Holland were especially adapted to this industry. In consequence a large quantity of linen was sent to that country to be bleached. One particular variety of linen that was bleached exclusively in Holland became known in the trade as "Hollands," a name retained to this day. Another variety of such fine texture that it was easily damaged, was spread on closely-cropped grass fields or lawns. Hence the name "lawn," which has survived the process.

In 1785, Bertholet discovered the bleaching power of chlorine. Immediately an attempt was made to bleach the linens by exposing them to the gas. This was effective in bleaching, but the gas also attacked the fiber. A solution of the gas in water was then tried. When the solution was of exactly the right concentration and with all other conditions favorable, fairly good results were obtained; but the process was attended with so much uncertainty that attempts were made to use the chlorine in some combined form. It was discovered in 1799 that dry slaked lime absorbs the gas in large quantities, and the compound thus formed has bleaching power. It is popularly known as "bleaching powder," and is now extensively used for bleaching linen, cotton, and other vegetable fabrics. It is not adapted to bleaching animal fibers, such as wool, silk, etc.

40. The Action of Chlorine on Hydrogen.—*In making the following experiment, place all apparatus under the hood and keep the hood closed as much as possible. Avoid inhaling the gas.*

EXPERIMENT 25. Employ the apparatus shown in Fig. 5, p. 25. Fit the tube D through a piece of card-board of sufficient size to cover the mouth of the cylinder. Generate a vigorous current of hydrogen in A, and, after five minutes, collect a test tube of the gas and take it four feet or more from the generator. If it burns quietly when lighted, ignite the gas at E and plunge the flame into the receiver F, which should be filled with dry chlorine, taking care that the card-board completely closes the cylinder. The flame continues, but with a peculiar whitish effect, and instead of water, dense white fumes are formed. The flame means that chemical action is taking place, and since two elements only are present, the chemical action must be a union of those elements. The product is a new chemical individual whose molecule must be

made up of at least one atom of hydrogen and one of chlorine. For the present we shall call it *hydrogen chloride*. Its composition may be expressed by the graph, $\text{H} + \text{Cl} = \text{H} \text{Cl}$,  though this experiment does not show that H and Cl combined atom for atom. (See Experiment 26). Withdraw the tube D from F without removing the cover, and note (1) the color, (2) the solubility in water, (3) the combustibility, (4) the power to support combustion, and (5) the odor of the gas in F. In noting the odor, inhale *only a very little* of the gas, for it is extremely irritating.

41. Properties of Hydrogen Chloride.—In the above experiment, hydrogen chloride is found to be a colorless gas possessing a suffocating odor. It is neither combustible nor a supporter of combustion, and it dissolves readily in water, imparting to it a sharp, sour taste. Its solubility in water may be shown by inverting the cylinder of gas over water, or by pouring some water into it and shaking.

42. Determination of the Formula of Hydrogen Chloride.—The method outlined in Experiment 25 throws much light on the composition of hydrogen chloride, but it is not well adapted for preparing it in quantity. This may be done by using the apparatus and process detailed in Experiment 26.

I. The decomposition of the hydrogen chloride by sodium amalgam.

EXPERIMENT 26.* *Caution! Perform this experiment under the hood.* A, Fig. 17, is a generating flask of 300 cc. capacity, which is provided with a funnel B and an exit tube D which is connected with C by a short rubber tube. C is filled with fused calcium chloride. E is a glass tube about 1.5 cm. in diameter and 60 cm. long, sealed at one end, and graduated into cubic centimeters.

* This Experiment should be performed by the teacher in the presence of the class. It is too difficult for most beginners.

Pour about 200 cc. of concentrated, commercial sulphuric acid into A, fill B with concentrated hydrochloric acid, connect the apparatus as shown in the illustration, and allow a little of the acid in B to run into A, drop by drop; dense fumes will be driven over into E. Stop the flow of acid, and examine the attributes of the fumes as to odor, and combustibility. It

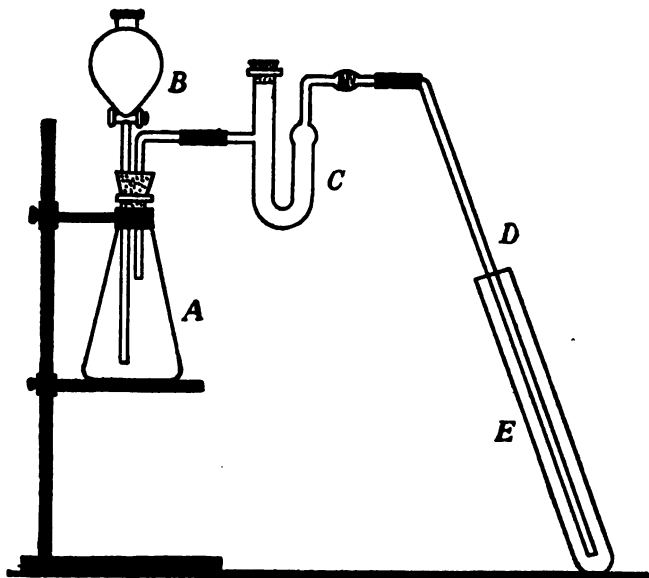
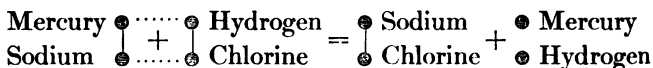


FIGURE 17

will be found that they possess the same attributes as the gas prepared in Experiment 25. It is hydrogen chloride which is being expelled from flask A.

Replace the delivery tube D so that it reaches quite to the bottom of E, heat the generating flask with a *small* flame, and allow the hydrochloric acid in B to run into A, one drop at a time. At first there will be a very copious evolution of gas. As this decreases in vigor, increase the heat cautiously, but the contents of A should not be heated to boiling. Continue the evolu-

tion of the gas until all air is expelled from the apparatus. (This is difficult to determine, though generally it is complete within 20 minutes. This is the most critical point in the experiment, for failure is generally due to the fact that all air is not expelled.) When all air is expelled, the tube will be filled completely with hydrogen chloride gas. When this is done, withdraw the delivery tube D very slowly while the gas still flows freely. Stopper the tube E quickly with a closely fitting rubber stopper. Have ready about 10 gm. of sodium amalgam* wrapped in tissue paper. Remove the stopper from E, drop the amalgam into the tube, and close it instantly and firmly with the rubber stopper. Invert the tube repeatedly until the amalgam is completely liquefied. This may require thirty minutes. During this process a white coating will be observed to collect upon the walls of the tube. This coating is due to the formation of common salt (see Experiment 23) and can mean only that the chlorine in the hydrogen chloride molecule has been withdrawn from it by the sodium in the amalgam. This may be expressed by the graph,



Did the hydrogen combine with the mercury? The following procedure will answer this question.

II. *Determination of the hydrogen in hydrogen chloride.*—Immerse the stoppered end of the tube E in a large cylinder of

*The amalgam may be prepared by the following process: *Caution! A flash occurs when the mercury and sodium are mixed. Keep the face away from the crucible. Have no rings on the fingers when handling mercury.*

Introduce 10 gm. of mercury into a 200 cc. iron or porcelain crucible, secure it in an iron ring which is firmly fastened to a ring stand, add 5 gm. of dried metallic sodium which has been cut into pieces about the size of a grain of corn, cover the crucible, and heat it with a small flame until a slight puffing or flash of light shows that vigorous action has begun. Withdraw the lamp instantly, allow the action to continue two or three minutes, then stir the contents vigorously with a glass or iron rod; pour the liquid mass into an iron or tin pan and let it solidify. So soon as solidification is complete, break up the product into small pieces and transfer it to a well-stoppered bottle; otherwise the moisture in the air will decompose it. This substance contains the mercury and sodium in a loosely combined state. It is an admirable medium for obtaining, without danger, the effects of metallic sodium.

water, A, Fig. 18, uncork it with the mouth of the tube under water, allow the excess of the amalgam B to sink to the bottom, clamp the tube so that its mouth will not be over the amalgam, and let it stand at least fifteen minutes. Adjust the tube so that the surface of the water in it coincides with the surface of the water in the cylinder, and read off the volume of gas.

If the experiment has been a success the volume of gas will be found to be about one-half of the volume of E. Now close the tube with the thumb, remove it from the cylinder, invert, and test the gas with a lighted match. It has all the attributes of hydrogen. It follows

that not all of the hydrogen combined with the mercury or sodium when the amalgam liquefied. Did any of it?

This may be determined as follows: Suppose the capacity of the tube E is 60 cc. There were then 60 cc. of hydrogen chloride vapor in it, *if all air was expelled*. The sodium of the amalgam combined with the chlorine to form common salt, which dissolved in the water of cylinder A. The combination of the chlorine created a vacuum, which was filled by the water. *Therefore the amount of water in E is a measure of the volume of chlorine which was in the hydrogen chloride vapor.* This was, e.g., 30 cc. The gas volume in the tube E also measured 30 cc. It follows that 60 cc of hydrogen chloride gas is composed of 30 cc. of hydrogen and 30 cc. of chlorine. Now these two volumes must contain, according to Avogadro's law, the same number of atoms. We know these atoms were *all combined*, for the original 60 cc. of gas was homogeneous and its

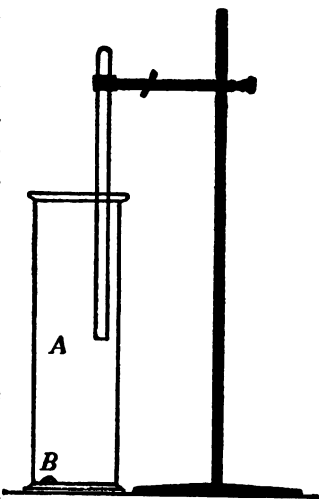


FIGURE 18

attributes were those of neither hydrogen nor chlorine. Therefore they must have been combined *atom for atom*, or in some multiple thereof. We may now write with authority the graph,



IODINE, I (AT. WT. 126.85)

The iodine of commerce is obtained chiefly from certain species of sea-weeds, which absorb small quantities of it from the sea-water. These weeds are collected, especially on the coasts of Ireland, Scotland, and France, and burned at a comparatively low temperature. The iodine compounds in the ash are dissolved with boiling water, and the solution evaporated to dryness. The residue is treated with manganese dioxide and concentrated sulphuric acid, as outlined in Experiment 27. The impure crystals are then re-vaporized and allowed to crystallize. The pure crystals have never been subdivided into substances which possess other attributes. Iodine is therefore classified as an element.

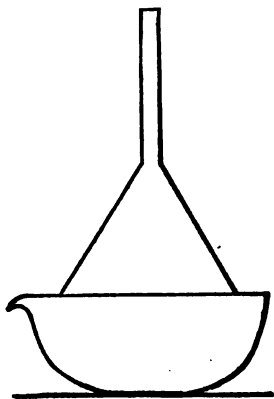


FIGURE 19

43. Preparation of Iodine.—

EXPERIMENT 27. Use the apparatus shown in Fig. 19. Mix and pulverize about 2 gm. each of potassium iodide, and manganese dioxide, place the mixture in the dish, moisten it thoroughly with concentrated sulphuric acid, place the funnel over it as shown in the cut, and apply a gentle heat to the bottom of the dish. A dense violet vapor will be set free, which, on cooling, will condense upon the sides of the funnel as a blue-black solid. Continue the heat until no more colored vapor is given off, invert the funnel, place a small cotton plug loosely

in the stem, and spray the sides with water until the crystals are washed. Drain thoroughly, place the crystals on a glass plate, and allow them to dry at the room temperature.

44. Properties of Iodine.—At the ordinary temperature iodine is a heavy crystalline solid, which vaporizes rather freely when exposed to the air, especially when moist. It is sparingly soluble in water, but dissolves readily in alcohol, to which it imparts a deep brown color. In chloroform it dissolves to a beautiful amethyst-colored fluid. It differs from all other elements in its peculiar property of forming a blue compound with ordinary starch. This property may be shown by adding a drop of iodine solution to a solution which contains starch paste (see Appendix).

Iodine is a much less active element than chlorine. It does not unite directly with hydrogen at ordinary temperature. Their union is effected only by indirect means, the product being hydrogen iodide, popularly known as hydriodic acid $\begin{array}{c} \text{H} \quad \text{I} \\ \bullet \quad \bullet \end{array}$

45. Hydrogen Iodide is a colorless, heavy, unstable gas of suffocating odor which dissolves readily in water. This solution has the general properties of hydrochloric acid. It is, however, much less stable, since it decomposes on long boiling or exposure to light and air, with the separation of free iodine, which gives to the ordinarily clear liquid a deep brown color.

NITROGEN, N (At. Wt. 14.04)

46. Preparation of Nitrogen.—*Caution! Always handle phosphorus with forceps and cut it under water. If held in the fingers, or cut in the air, it may ignite and produce deep and painful burns.*

EXPERIMENT 28. Fill the pneumatic trough A, Fig. 20, with sufficient water to cover the stage D to the depth of at least 5 cm., place a piece of phosphorus about the size of a

bean in the crucible C, float it over the stage, ignite the phosphorus and depress the cylinder B over it so that the mouth of the cylinder will be submerged while resting on the stage.

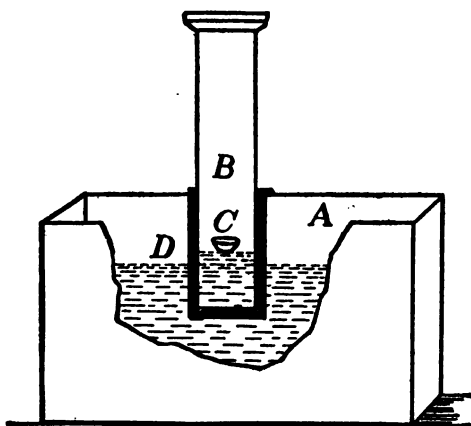


FIGURE 20

The phosphorus will continue to burn with the evolution of dense white fumes which are soluble in water. Let the cylinder stand undisturbed until its contents are colorless. Invert the cylinder, using a glass plate cover, measure the height to which the water has risen in it, and then test the gas

in the upper part as to color, odor, solubility in water, combustibility, and power to support combustion. When pure the gas has no odor, but there will probably be an odor here, because of the presence of some unburned phosphorus.

47. Properties of Nitrogen.—If the experiment is successful, a colorless and comparatively odorless gas is obtained which neither supports combustion, nor is itself combustible. It was pointed out in Experiment 11 that carbon dioxide also possesses these attributes. We must look to some other attribute to identify it. It was shown in Experiment 18 that carbon dioxide dissolves readily in a solution of caustic soda. Prepare a second receiver of the gas as above directed, invert it over such a solution and let it stand over night; the volume of gas will be observed to have remained unchanged. This shows that the gas is not carbon dioxide. The principal constituent of this gas is *nitrogen*.

Nitrogen was discovered by Rutherford in 1772, but it was Lavoisier who showed its elementary character and its relation to the atmosphere. That it is a constituent of the atmosphere was shown in the above experiment. The cylinder B was filled with air. The phosphorus removed the oxygen, and left the nitrogen unchanged. This fact suggests its chemical inactivity.

Nitrogen combines directly with none of the common elements excepting magnesium, boron, silicon, and titanium. Its union with other elements is effected by indirect means, and the resulting compounds are usually unstable. Some of these unstable compounds are used in the preparation of such explosives as gunpowder, nitroglycerine, picric acid, and guncotton.

48. The Relation of Nitrogen to Life.—When undiluted nitrogen is taken into the lungs, it suffocates by excluding the life-supporting oxygen. It is not, however, a poison. Indeed it is an essential constituent of all animal and plant tissue. Animals can not appropriate it directly from the air, but derive it from their food, especially from *albumen*, which is found in the tissues of plants and animals. Plants appropriate simple compounds of nitrogen, e.g., saltpeter, and from them derive the nitrogen which enters into albumen. Animals can not do this, but depend upon the nitrogenous compounds formed by plants. A fuller discussion of the importance of nitrogen compounds to higher life will be given later.

49. Composition of the Air.—Since we have studied two of the most important constituents of the air, viz., oxygen and nitrogen, it is desirable to study the air a little more fully. The approximate proportion of these two elements may be shown in this wise:

EXPERIMENT 29. *Caution! Handle phosphorus with care.* A, Fig. 21, is a graduated tube; B is a piece of phos-

phorus held in place by a bent iron wire C; D is a beaker containing water. Partly fill the tube A with water, close it with the thumb, invert it in the water in D, and fasten it in

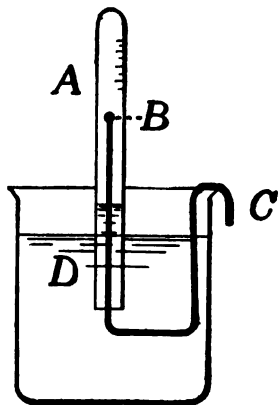


FIGURE 21

place with a clamp. There will now be air in the upper part of the tube A. Record the volume of this air. Through the water insert the wire with the phosphorus attached, so that the phosphorus will come nearly to the top of the tube, fasten the supporting wire firmly in position, and let the apparatus remain undisturbed for 24 hours, and then read the gas volume. Meantime, the phosphorus will have combined slowly with the oxygen, and the product of the union will have been absorbed by the water. The so-

lution of this gas, which contains the oxygen which was in the air, is what causes the water to rise, and its rise thus becomes a measure of the subtracted oxygen. Suppose the original volume of air

= 50 cc.

The remaining volume will be about

= 40 cc.

10 cc.

10 cc. therefore = the volume of oxygen in 50 cc. of air.

The properties of the oxides of nitrogen lead one to believe that the air is a mixture, and not a combination of nitrogen and oxygen, for all of the nitrogen oxides possess poisonous properties.

Since, as was pointed out in Experiment 15, carbon dioxide is the final product of the combustion of carbon in oxygen, carbon dioxide must be given off in immense quantities* from

* Strasburger estimates that the human species expires 1,200 million kilograms of carbon dioxide every 24 hours; and that 1,265,000 million kilograms of the gas is given off yearly from the combustion of carbon in furnaces.

coal and wood fires. That carbon dioxide is present in the air, especially in localities which are manufacturing centers, is shown by analytical investigations. In town air the quantity varies from $3\frac{1}{2}$ to 7 parts in 10,000; i.e., 10,000 cubic feet of air contains from $3\frac{1}{2}$ to 7 cubic feet of carbonic acid gas. Country air contains about $3\frac{1}{2}$ parts per 10,000. Over the sea the proportion is slightly less.

The vapor of water is another constituent of the air. Hydrogen, ammonia, and the gases argon, krypton, neon, and xenon are present in minute quantities. The last four gases were unknown to science until 1895, when Lord Raleigh and Professor Ramsey discovered argon, a colorless, odorless gas which constitutes about .94 per cent of the air, as a constituent of what had been regarded as atmospheric nitrogen. It is even more inactive than nitrogen, and as yet has not been combined with any other element. The other three elements mentioned above also occur in minute quantities, and, like argon, are very inactive. As yet these four elements are not of recognized importance. All of these subordinate constituents make up but a very small part of the atmosphere. Since oxygen is about one-fourth of the atmosphere it follows that most of the remainder is nitrogen.

COMPOSITION OF THE AIR BY VOLUME (AVERAGE)

Nitrogen.....	78.85	Argon.....	0.94
Oxygen.....	20.77	Ammonia.....	traces
Water Vapor.....	0.84	Other Elements.....	"
Carbon Dioxide.....	0.03		

Small quantities of solids are also present, e. g., ammonium nitrate, ammonium carbonate, common salt, dust, etc.

The preceding table gives ammonia as one of the minor constituents of the air. It is, however, one of the most important compounds of nitrogen with which the chemist has to deal; hence it should be studied in detail.

50. Preparation of Ammonia.—EXPERIMENT 30. Use the apparatus shown in Fig. 16, Experiment 22. Mix intimately about 10 gm. each of sal-ammoniac (ammonium chloride) and slaked lime, bring the mixture into the generating flask A, add about 10 cc. of water, connect the apparatus as shown in the figure, apply a gentle heat to A, and collect the gas by upward displacement. It is lighter than air and therefore cannot be collected by downward displacement. Note its odor, color, combustibility, and its power to support combustion.

51. Properties of Ammonia.—Ammonia is a colorless gas which possesses a characteristic pungent odor familiar to all. Its properties were known to the ancients, by whom it was called “vehement odour”; but Priestley first separated it in a pure form in 1774, and called it “alkaline air.” It is formed during the decay of plant and animal tissues and passes into the atmosphere, where it is speedily absorbed by the moisture. It is also a product of the dry distillation of nitrogenous substances.

Its extraordinary solubility in water may be shown by inverting a receiver of it in water. On removing the plate the water will rush up into the receiver, sometimes with great force. If the receiver contains no air, the water will completely fill it. One cubic centimeter of water at the ordinary temperature of the laboratory will dissolve about 740 cc. of the gas. This solution is commonly called *aqua ammoniae*, ammonia water, or hartshorn. The last name was given to it from the fact that in very early times it was prepared by distilling the horns of the deer (hart), and dissolving the product in water. It is now obtained in quantity from the ammoniacal waters of gas works. When coal is strongly heated in a closed vessel, illuminating gas and ammonia are driven off. The ammonia is dissolved in the water through which the gas is washed, and this water is the “raw material” from which most ammonia is obtained.

The commercial aqua ammonia^{ae}, also called ammonium hydrate or ammonium hydroxide, which contains from 10 to 30 per cent of ammonia gas, possesses the characteristic pungent odor of ammonia, because at ordinary temperature the gas escapes from the solution. It can be quickly and completely expelled by boiling, showing that if the ammonia is in chemical union with the water, the compound is exceedingly unstable. Water which contains approximately 30 per cent of the gas is an exceedingly strong corrosive to all mucous tissues.

52. Composition of Ammonia.—The constituents of ammonia may be determined in the following manner:

I. A current of ammonia gas, obtained as in Experiment 30, is dried and passed into a tube containing heated metallic potassium. The end of this tube dips into the pneumatic

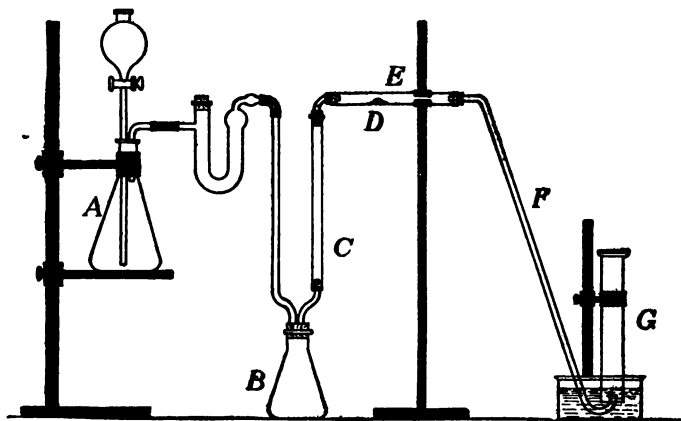


FIGURE 22

trough, and from the end gas is collected and allowed to stand some time. This gas is shown by the usual tests to be hydrogen. Hence hydrogen is one of the elements of which ammonia is composed. During the experiment the potassium becomes dark in color.

II. Into a tube of dry chlorine gas, obtained as in Experiment 22, ammonium hydrate is allowed to drop. Dense white fumes form and disappear when the tube is inverted over water, leaving a colorless gas, which possesses all the attributes of nitrogen. Hence nitrogen is one of the elements of ammonia. The volume of the nitrogen is measured in the way described in Experiment 26.

I. The qualitative composition of ammonia may be determined in the following manner. The apparatus shown in Fig. 22 will serve for the first part of the determination.

EXPERIMENT 31. A is an ordinary 300 cc. flask which is provided with a good cork and a glass delivery tube connecting it with C. This is a piece of glass tubing about 30 cm. long and 1.5 cm. in diameter. It should be loosely filled with unslaked lime, excepting near the ends, where plugs of cotton hold the lime in place. Flask B is an ordinary flask, also filled in part with unslaked lime. The only purpose of these two pieces is to remove all the moisture from the gas as it is led in from A to D. E is a piece of glass of difficult fusibility about 30 cm. long and 1.5 cm. wide, which is provided with a one-holed stopper at each end, connected respectively with C and F. F is a piece of glass tubing bent so as to connect conveniently with the cylinder G, which serves to receive the gas.

Mix intimately about 50 gm. each of slaked lime and ammonium chloride, bring the mixture into the generating flask A, connect B, C, and E as shown in the cut, and apply a gentle heat to A. A vigorous flow of concentrated ammonia vapor will be given off, and should be maintained until all air is expelled from the apparatus. Complete expulsion of the air can be determined by collecting some of the gas escaping from F in a test-tube filled with water (Experiment 6, p. 23). If a residual gas, insoluble in water, remains, air is still present in A. When it has been completely expelled, introduce a piece of clean, dry, metallic potassium into E at

D, connect F with E and G, as shown in the cut, and heat the tube at D until the potassium fuses.* Maintain the potassium in a fused state while the ammonia gas passes over it for at least ten minutes, or until the receiver G is filled with gas. The melted potassium will be observed to assume a grayish-black color, which indicates that a chemical action has taken place between it and the ammonia. Interrupt the process, loosen the discolored potassium with a dry glass rod, stopper it securely in a clean and perfectly dry flask, and keep it for further use.

Now examine the gas in G as to odor, combustibility, and power to support combustion. Its odor will be obscured by the presence of ammonia which passed over into G and was absorbed by the water. This difficulty may be obviated by inverting the cylinder G over a large cylinder of fresh water until all ammonia is absorbed. The residual gas in G will be found to be hydrogen. This must have been derived from the ammonia, for potassium is an element. It follows that ammonia is a compound gas which contains hydrogen within its molecule. The other constituent will be determined in the next experiment, which should be performed under the hood, using the apparatus shown in Fig. 23.

II. *The quantitative composition of ammonia.*

EXPERIMENT 32. Flask A, Fig. 23, with its separating funnel B and delivery tube C, is essentially a duplication of that used in Experiment 6. The point D of the delivery tube C should be curved sharply upward. Generate a vigorous flow of chlorine from A, as directed in Experiment 22, which must be maintained until all air is expelled from the flask and delivery tube. To prevent chlorine from escaping into the air, keep the end of the delivery tube immersed in a solution of caustic soda, which absorbs the gas very readily. To discover when all air is expelled, fill a shallow dish of at least 10 cm.

* *Caution! Handle potassium carefully, for it ignites instantly when it touches water. Handle with pincers, and see that all parts of the apparatus which it may touch are thoroughly dry.*

in diameter two-thirds full of the soda solution, invert into it a test-tube also filled with the same solution, bring the point of the delivery tube C under the mouth of the test-tube, and let

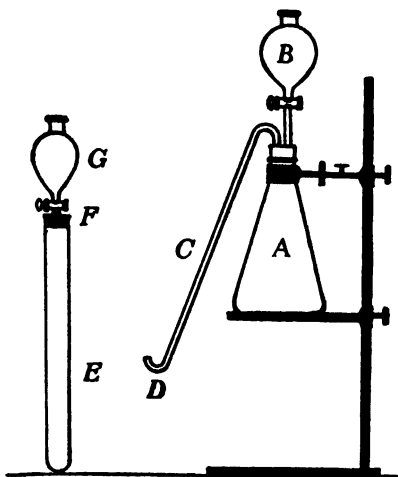


FIGURE 23

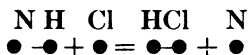
the chlorine stream into it for two or three minutes. Remove the tube C, stopper the test-tube with the thumb, invert it five or six times to insure the absorption of any chlorine in the upper part of the tube, again immerse the mouth of it and remove the thumb. When the soda solution fills the test-tube completely, it shows that there is no air in the escaping gas. If the flow of chlorine slackens before this point is reached, add

small amounts of acid from B. When all air is expelled from A, fill the graduated tube E with chlorine after the manner adopted in collecting hydrogen in Experiment 6. While the chlorine is collecting, fill the funnel G with concentrated ammonium hydrate, open the stopcock, and allow the liquid to fill the stem F (which should not be more than 6 cm. long) of the funnel G. It should pass through a one-holed rubber stopper which fits the graduated tube E very snugly.

Stopper the tube E with the thumb, invert it, and quickly insert and firmly set the rubber stopper carrying the funnel G. Dense white fumes will be formed in E, sometimes attended with a flash of yellow light; the tube E will be considerably heated, and should be cooled with a spray of cold water. Now allow the ammonia to drop into E, keeping the tube cool with the water spray, until at least 10 cc. have been added. Close

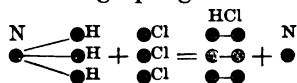
the stopcock, remove the excess of ammonia in G, and shake the contents of E for five minutes; cool the tube, fill the funnel with dilute sulphuric acid (1 : 10), and allow it to run into E until it ceases to flow freely, being careful the while to keep the contents of the tube well cooled. Be careful not to allow any of the gas to escape through the stopcock into G. Now invert E over water, remove the stopper, let stand fifteen minutes, and read off the volume of gas after the manner described in Experiment 26, Fig. 18. Test the gas for nitrogen. (See Experiment 28.)

When the ammonia was dropped into the chlorine in E, the hydrogen of the ammonia combined with the chlorine to form hydrogen chloride and this quickly dissolved in the water. The nitrogen was set free. These changes may be expressed by the graph,



which is qualitative but not quantitative.

The *proportion of combination* may be determined by the following considerations. Suppose the volume of E = 60 cc.; there were then 60 cc. of chlorine in the tube before any ammonia was added. All of this chlorine combined with the hydrogen of the ammonia to form hydrogen chloride, for the residual gas did not possess *any* of the attributes of chlorine. This must have required 60 cc. of hydrogen (see p. 61), and this 60 cc. must have been withdrawn from the ammonia. Suppose the volume of nitrogen obtained was 20 cc.; this must have been set free *in direct proportion to the withdrawal of hydrogen from the ammonia molecule*. It follows that 60 cc. of hydrogen were combined with 20 cc. of nitrogen, which, according to Avogadro's law, gives an atomic ratio of 3 : 1, or some multiple thereof. We may now reconstruct the graph given above. We shall have,



It is customary to condense this into the expression, $\text{NH}_3 + 3 \text{Cl} = 3 \text{HCl} + \text{N}$. This means that the three atoms of hydrogen in the ammonia molecule combined with three atoms of free chlorine to form three molecules of hydrogen chloride, while one atom of nitrogen was set free.

What would be the interpretation if 23 cc. of nitrogen were found instead of 20 cc.? The ratio would be 60 cc. H : 23 cc. N. Accepting Avogadro's law, there would be $2\frac{1}{3}$ atoms of hydrogen for each atom of nitrogen, which contradicts the atomic theory. Let us consider the meaning of this result, 60 cc. H : 23 cc. N, from another point of view. If the formula were

NH_4 ,	the proportion of the gases would be	15 cc. N : 60 cc. H	Errors 8 cc.
NH_5	" " " "	12 cc. N : 60 cc. H	" 11 cc.
N_2H_3	" " " "	40 cc. N : 60 cc. H	" 17 cc.
N_2H_4	" " " "	30 cc. N : 60 cc. H	" 7 cc.
N_2H_5	" " " "	24 cc. N : 60 cc. H	" 1 cc.
N_2H_6	" " " "	20 cc. N : 60 cc. H	" 3 cc.
N_2H_7	" " " "	17.11 cc. N : 60 cc. H	" 5.9 cc.

It will be noted that the discrepancy between the *observed* and the *theoretical* quantity of nitrogen decreases as the proportion of the two gases approaches the hypothetical structure N_2H_5 , or some multiple of it, and increases as it departs from this formula. This means either that the true formula for ammonia is N_2H_5 (or some multiple of it), or that the experimental results were not correct. Any source of error may be eliminated by repeating the experiment several times and taking the average of the results. Suppose three experiments gave:

21 cc. N : 60 cc. H (1)

20 cc. N : 60 cc. H (2)

20 cc. N : 60 cc. H (3)

Average 20.3 cc. N : 60 cc. H

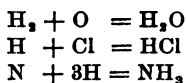
It has been the experience of many that the average of several estimates approximates very closely to 1 Vol. N : 3 Vol. H, which gives the formula, NH_3 .

Fortunately we are able to determine the molecular weight of a gaseous molecule, i.e., NH_3 , by observing the relation of its density to its molecular weight. It is proposed to develop in the succeeding pages a notion of this relation and how it may be used to determine the weight of a molecule.

53. The Relation of the Density of a Gaseous Element to its Atomic Weight.—Before taking up a discussion of this relation, it will be helpful to summarize the data upon which its interpretation is based:

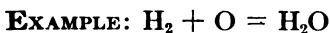
1. Copper, zinc, iron, hydrogen, oxygen, chlorine, bromine, iodine, carbon, and sodium are elements. Every atom of each element possesses exactly the same attributes as every other atom of that element. These atoms are mutually interchangeable.

2. Such substances as water, hydrogen chloride, ammonia, carbon dioxide, hydrogen sulphide, etc., are made up of at least two kinds of elements which are intimately combined:



The unit of such a compound is the molecule. Any molecule of a given compound possesses all the attributes of any other molecule. These molecules are therefore mutually interchangeable. One molecule of water, H_2O , has all the chemical attributes of water, and is therefore as representative of the qualities of that substance as an inconceivably large quantity would be. Salt is salt, whether it be .000001 gm. (see Experiment 3), or a ton.

3. The molecular weight is equal to the sum of the weights of the atoms.



$$2 + 16 = 18, \text{ the molecular weight.}$$

4. Density = $\frac{\text{mass}}{\text{volume}}$, is therefore a ratio and not an absolute quantity.

When the volumes of different gases are equal, their densities are directly proportional to their masses. For example, let the cylinders A, B, and C (Fig. 24) have equal volumes, for

example, 60 cc. Let A be filled with hydrogen, B with chlorine, and C with nitrogen, all under the same conditions of tempera-

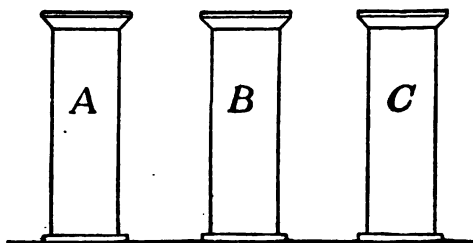


FIGURE 24

ture and pressure. Suppose the weights of the gases are respectively .0048 gm., .1704 gm., and .0672 gm.

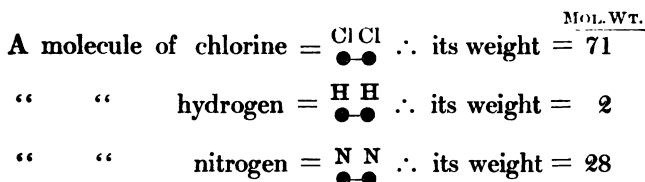
These weights* represent the masses of equal volumes of

H, Cl, and N. Dividing the weights by .0048 to simplify the numerical expression, we have, 1, 35.5, and 14. This means that if the mass of a given volume of hydrogen be taken as 1, then the mass of equal volumes of Cl and N are 35.5 and 14 respectively. Now 1, 35.5, and 14 represent the atomic weights of these elements. Hence the density of an elementary gas is the same as its atomic weight (H = 1 being the standard).

	If the density of H = 1
then	" " " Cl = 35.5
	" " " O = 16
	" " " N = 14
and	" " " Br = 80

54. Density and Molecular Weight of an Elementary Gas.—It will be shown in the succeeding pages that the molecule of a *simple gas* is made up of *two atoms*.

*The above method for determining the respective weights of equal volumes of gases is not used in practical work. It would be inconvenient, because the cylinders would need to be very large to contain any appreciable weight of gas. It would also be difficult to fill and seal them without error. The methods used in actual practice follow this principle, but are too complicated for description in this work.



From the foregoing, the following law may be formulated: The number expressing the density of an *elementary* gas is *identical* with its *atomic* weight, and *one-half* of its *molecular* weight.

55. Density and Molecular Weight of a Compound Gas.—Does a definite relation exist between the molecular weight and the density of a *compound* gas? The observed densities of water vapor, hydrogen chloride, and ammonia are respectively 9, 18.25, and 8.5.

Hence, we have.

DENSITY	FORMULA	MOL. WEIGHT
9	H ₂ O	18
18.25	HCl	36.5
8.5	NH ₃	17.0

The density of each of these gases is one-half its molecular weight. Indeed, the law has been established that the density of *any* gas, whether simple or compound, is equal to one-half its molecular weight. This remarkable relation between density and molecular weight is grounded in what is called the “two-volume law.”

56. Density, and the “Two-Volume Law.”—It has been established by careful observations that when unit volumes, e.g. 100 cc., of two gaseous elements unite to form a molecule, *two volumes* of the new gas are always formed. This is illustrated in the following table:

TABLE I

2 vols.	H	+	1 vol.	O	=	2 vols.	H ₂ O (vapor)
3 "	H	+	1 "	N	=	2 "	NH ₃
2 "	N	+	1 "	O	=	2 "	N ₂ O
2 "	N	+	3 "	O	=	2 "	N ₂ O ₃
1 "	H	+	1 "	Cl	=	2 "	HCl
1 "	H	+	1 "	H	=	2 "	H ₂

No satisfactory explanation for this remarkable department has ever been given. Now let the law be applied to the interpretation of density.

EXAMPLE 1. $\left(\begin{smallmatrix} 2 \text{ vols. H, weight } 2 \\ 1 \text{ " O, " } 16 \end{smallmatrix} \right) = 2 \text{ vols. H}_2\text{O, weight 18;}$

$\therefore$ since two volumes of water vapor weigh 18, one volume weighs 9, and since the weight of a unit volume represents the density, the density of water vapor is 9 (density of H = 1).

EXAMPLE 2. $\left(\begin{smallmatrix} 3 \text{ vols. H, weight } 3 \\ 1 \text{ " N, " } 14 \end{smallmatrix} \right) = 2 \text{ vols. NH}_3, \text{ weight 17;}$

$\therefore$ since the weight of two volumes of NH₃ is 17, the weight of a unit volume is 8.5. Hence the density of NH₃ is 8.5 (H = 1).

EXAMPLE 3. $\left(\begin{smallmatrix} 1 \text{ vol. Cl., weight } 35.5 \\ 1 \text{ " H, " } 1 \end{smallmatrix} \right) = 2 \text{ vols. HCl, wt. } 36.5;$

Hence the density of HCl is 18.25 (H = 1).

57. Density, and Avogadro's Law.—It has been seen above that for like volumes of gases under the same conditions of temperature and pressure, the numerical value of density and mass is the same. Now the mass of a given volume of a compound gas must be equal to its molecular weight multiplied by the number of molecules in that volume. For convenience let the number of molecules be represented by Y; then we have,

Mass = Mol. Wt. $\times$ Y. By substituting Density for Mass, we have Density = Mol. Wt. $\times$ Y.

By substituting the different observed values for density given on p. 77, we have:

DENSITY		MOL. WT.		RATIO OF MOLECULES
9	 H_2O	18	...then	$9 = 18 Y, \therefore Y = \frac{1}{2}$
18.25	 HCl	36.5	..	$18.25 = 36.5 Y, \therefore Y = \frac{1}{2}$
8.50	 NH_3	17.0	..	$8.5 = 17 Y, \therefore Y = \frac{1}{2}$

Y has the same value for each. Now Y represents the *relative* number of molecules in equal volumes. Therefore if a given volume of hydrogen has Y molecules, then, under similar conditions, like volumes of all other gases, whether simple or compound, will contain an equal number of molecules.

This is Avogadro's law, the law referred to on page 78, and it is of great importance in determining the formula of a compound gas.

58. Avogadro's Law, and Formulas.—In Experiment 10, sulphur and hydrogen combined to form hydrogen sulphide. In Experiment 15, carbon and oxygen combined to form carbon dioxide; but in neither case was the proportion in which the atoms combined determined.

The observed density of the two gases is as follows:

Density of hydrogen sulphide = 17 (1).

Density of carbon dioxide = 22 (2).

Since the density of a gas equals one-half its molecular weight, the molecular weight of hydrogen sulphide is 34, and of carbon dioxide, 44.

The atomic weight of sulphur is 32. Since molecular weight of a substance is always equal to the sum of its atomic weights, and since there must have been at least one atom of sulphur in the hydrogen sulphide molecule, $\frac{32}{34}$ by weight of the hydrogen sulphide molecule must be sulphur, and the remaining $\frac{2}{34}$ hydrogen. Since the atomic weight of hydrogen

is taken as unity, the $\frac{2}{34}$ must represent two atoms of hydrogen. Hence the formula, H_2S .

The atomic weight of carbon is 12. The synthesis of carbon dioxide shows that its molecule contains carbon and oxygen only. Its density indicates that the molecular weight is 44. Different possibilities suggest themselves. For example:

1. If the molecule of carbon dioxide contains two atoms of carbon, the weight of the carbon in the carbon dioxide molecule is 24, and the remaining 20 units ($44 - 24 = 20$) of weight must be the weight of the oxygen atoms. Since one atom of this element weighs 16, $1\frac{1}{2}$ atoms would be required. We cannot accept this as representing the fact without laying aside the atomic theory, which we have every reason to believe is true.

2. If the molecule contains but one atom of carbon, the weight of the carbon in the carbon dioxide molecule is 12, and the weight of the oxygen 32 ($44 - 12 = 32$), 32 is twice the atomic weight of oxygen. On this basis $\text{C} + \text{O}_2 = \text{CO}_2$, and this is in accord with the atomic theory, and is accepted as the true formula.

59. The "Two-Volume Law," and the Molecular Theory of Gases.—The "two-volume law" and its relation to Avogadro's law, throws much light upon the nature of all elementary gases.

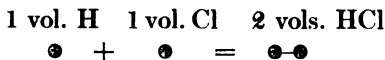
A comparison of the density of elementary gases with the density of compound gases, suggests that the former are made up of molecules of two atoms each.

Density of H	= 1.0	} Experimental values.
" " CO ₂	= 22.0	
" " Cl	= 35.5	
" " H ₂ S	= 17.0	
" " H ₂ O	= 9.0	
" " NH ₃	= 8.5	

Since the observed density of the compound gas is in every case equal to one-half of its molecular weight, and the observed density of an elementary gas is equal to its atomic weight, we infer that each molecule of the elementary gas contains *two atoms* of the element. The "two-volume law" points to the same conclusion. We have discovered that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. If these unit volumes are 100 cc. each, we have,



According to Avogadro's law, unit volumes of elements contain *the same number of atoms*. We have,



This indicates that the molecule of HCl occupies twice the space occupied by an atom of hydrogen or chlorine. As this seems logical enough, let us apply this interpretation to three other cases. Experiment has shown

1. That $\left(\begin{array}{ccc} 2 \text{ vols.} & 1 \text{ vol.} & 2 \text{ vols.} \\ \text{H} & + & \text{O} \end{array} = \text{H}_2\text{O} \right)$
2. " $\left(\begin{array}{ccc} 3 \text{ vols.} & 1 \text{ vol.} & 2 \text{ vols.} \\ \text{H} & + & \text{N} \end{array} = \text{NH}_3 \right)$
3. " $\left(\begin{array}{ccc} 2 \text{ vols.} & 3 \text{ vols.} & 2 \text{ vols.} \\ \text{N} & + & \text{O} \end{array} = \text{N}_2\text{O}_3 \right)$

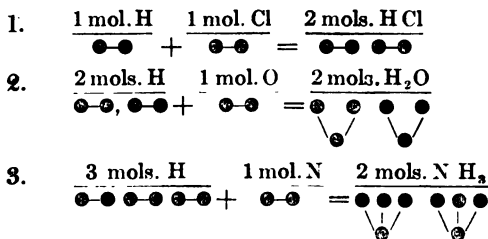
Applying the interpretation which was given to the formation of two volumes of hydrogen chloride from one volume of hydrogen and one volume of chlorine, we should expect:

THEORETICAL.

1. $\left(\begin{array}{ccc} 2 \text{ vols.} & & 1 \text{ vol.} \\ \text{H} & + & \text{O} \end{array} \right) = \text{H}_2\text{O} \quad 3 \text{ vols.}$
2. $\left(\begin{array}{ccc} 3 \text{ vols.} & & 1 \text{ vol.} \\ \text{H} & + & \text{N} \end{array} \right) = \text{NH}_3 \quad 4 \text{ vols.}$
3. $\left(\begin{array}{ccc} 2 \text{ vols.} & & 3 \text{ vols.} \\ \text{N} & + & \text{O} \end{array} \right) = \text{N}_2\text{O}_3 \quad 5 \text{ vols.}$

As stated above, the experimental result is two volumes in each case.

What is the significance of this inconsistency? It is important to note that, temperature and pressure being the same, the molecules of all compound gases occupy equivalent spaces, regardless of the number of atoms which compose them. With this fact established, let us seek for an explanation of the two-volume behavior. If the elementary gases consist of molecules of two atoms, we should have,



It is apparent that the theory that the molecules of elementary gases contain two atoms, is in harmony with the experimental results.

60. The Molecular Theory of Gases, and "Nascent Elements."—This theory is reinforced by another well known phenomenon, viz., that elements at the instant they are set free from combination are much more active chemically than afterward. This is explained by the theory that an element, at the instant it is liberated from combination is in the *atomic* condition and that in this condition it is more active than when its atoms are combined into molecules. An element is said to be "nascent" at the instant it is liberated from combination, and, accordingly, "atomic condition" and "nascent condition" are synonymous terms.

The density, "two-volume" constant, and activity of elements in the atomic state tend to corroborate the theory that the molecules of elementary gases consist of two atoms.

61. Nascent Elements, and Ozone.—One of the few exceptions to the preceding theory, that molecules of elementary gases have two atoms, is met with in a peculiar modification of oxygen called ozone, discovered in 1840 by Schönbein, who described its peculiar properties. It may be obtained from oxygen in various ways. It is generally produced in the electrolysis of water, the oxidation of phosphorus, the combustion of hydrogen, and during the discharge of electricity from a Holtz machine or a Ruhmkorff's coil. Its presence in the air is detected by exposing a strip of paper moistened with a starch solution to which a little potassium iodide has been added. Ozone gives to this paper a characteristic indigo-blue color. (Compare iodine.)

62. Preparation of Ozone.—**EXPERIMENT 33.** Place three or four pieces of clean yellow phosphorus in a porcelain boat, moisten them with a water solution of potassium bichromate, introduce the boat with its contents into a glass tube of suitable size, pass oxygen obtained as in Experiment 9 through it until the air is practically expelled, stopper the tube and allow it to stand ten hours. Now test this atmosphere for ozone with the "potassium iodide-starch" solution.

63. Ozone Is a Form of Modified Oxygen.—That ozone is a modification of oxygen may be shown as follows: A, (Fig. 25) is a beaker containing dilute sulphuric acid (1.20); B is a glass tube about 3 cm. in diameter having an opening at E and drawn out to a point at D; within this is a test-tube C of sufficient size to leave only a narrow air space between the walls of the two tubes. The tube C is filled two-thirds full of dilute sulphuric acid, and the platinum or copper wire F is adjusted so that it reaches nearly to the bottom of the tube. This

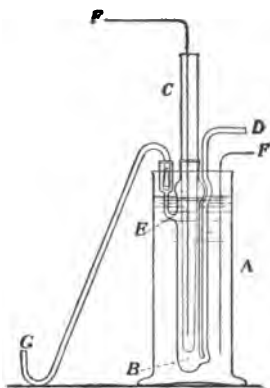


FIGURE 25

wire is connected with one pole of a Ruhmkorff's induction coil, and F', which dips into the sulphuric acid in A, is connected with the other pole. When a slow stream of oxygen is passed through the tube B, from G to D, while the induction coil is in action, the gas as it issues from D will possess the attributes of ozone. The construction of the apparatus is such that only oxygen is admitted into B; it follows that ozone is some modification of this element.

64. Structure of Ozone.—The nature of this modification may be interpreted from the following data:

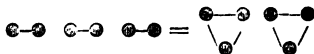
3 vols. of oxygen contract to 2 vols. of ozone.

2 vols. of ozone expand to 3 vols. of oxygen, when heated.

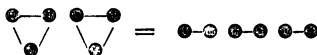
The density of ozone is 24. ($H = 1$.)

The meaning of the first two values is simple enough, if we accept the theory that elementary gases exist in molecules. We should have,

a. 3 vols. O; 2 vols. of ozone.



b. 2 vols. ozone; 3 vols. of oxygen.



c. Since molecular weight = density $\times 2$, we have 48 as the molecular weight of this peculiar substance. This confirms the assumption in *a* and *b*, i. e., that the molecular structure is O_3 . It may be viewed as oxidized oxygen. Certainly it is a modification of that element.

Summary.—It has been pointed out in the preceding pages that:

1. Atoms may combine to form very stable molecules which possess characteristic attributes, and are therefore chemical individuals.

2. Any molecule of the new compound possesses all the attributes of all the others. They are therefore mutually interchangeable.

3. When the product is a gas, a given volume of it contains the same number of molecules as a like volume of any other gas measured under the same conditions of temperature and pressure.

4. The density of any gas is always one-half its molecular weight.

FORMING.

5. Hydrogen and chlorine combine in ratio of 1 : 1, HCl

Hydrogen " oxygen " " " " " 2 : 1, H₂O

Hydrogen " nitrogen " " " " " 3 : 1, H₃N

Carbon " oxygen " " " " " 1 : 2, CO₂

Hydrogen " sulphur " " " " " 2 : 1, H₂S

EXERCISES.

1. A molecule of turpentine is C₁₆ H₁₆; would you expect it to burn in an atmosphere of chlorine? Would the flame be smoky?

2. Is sodium amalgam a mechanical mixture?

3. How may the hydrogen be withdrawn from the hydrogen chloride molecule?

4. A sample of baking powder turned blue when it was moistened with a solution of iodine. What does this indicate?

5. The density of hydrogen chloride is 36.5. What is the structure of its molecule?

6. Determine the weight of the molecules from the following densities:

D. of water vapor = 9

" " carbon sulphide = 38

" " " dioxide = 22

" " nitrogen hydride . . . = 8.5

7. How many cc. of gas will be made by the union of:

1. 200 cc. hydrogen and 100 cc. oxygen

2. 200 cc. nitrogen " 500 cc. "

3. 200 cc. hydrogen " 200 cc. chlorine

4. 200 cc. " " 200 cc. oxygen

8. Would Avogadro's law hold if it were shown that $D = \frac{\text{Mol. Wt.}}{2}$ is not true?

9. Is this law more than a working hypothesis?

10. Is the evidence upon which the demonstration of Avogadro's law is based, theoretical or experimental?

CHAPTER V

FORMULAS AND DEFINITE PROPORTIONS

The following formulas were established in the preceding chapter: HCl , H_2O , H_3N , CO_2 , and H_2S . It will be observed that in these formulas both the hydrogen atom and the oxygen atom enter into combination in varying proportions. It is the purpose of this chapter to show that atoms always combine in *definite* proportions.

65. The Deportment of Magnesium toward Hydrogen Chloride is an Illustration.

EXPERIMENT 34. A (Fig. 26) is a 200 cc. Erlenmeyer flask provided with a rubber stopper with two perforations; one is

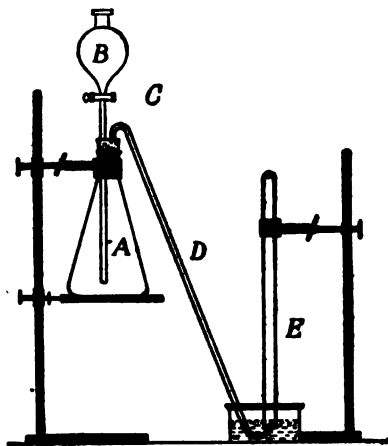
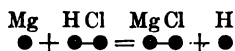


FIGURE 26

fitted with a separatory funnel B, the other with a right-angled tube D, which should not extend below the lower inner surface of the stopper. Connect this arm with the inverted tube E, which should be graduated into tenths of a cubic centimeter, and be of at least 100 cc. capacity. Rub a piece of magnesium ribbon with sandpaper until it is perfectly bright, weigh accurately about 0.1 gm., tie it to a piece of glass to weight it, put it into the flask A, set the stopper firmly, and add water from the separatory funnel until the whole apparatus is com-

pletely filled with it. All air must be expelled. The upper level of the water in B should not be allowed to pass below C; otherwise air will be admitted into the apparatus. Fill the tube E with water, invert, connect the whole apparatus as shown in the cut, fill the funnel B with dilute hydrochloric acid (1 : 3), and allow about one-third of it to flow into the flask A. Hydrogen will be evolved energetically.

Let the action continue until the magnesium is completely dissolved. To drive all hydrogen into E, pass 200 or 300 cc. of water through the apparatus, taking care to prevent the ingress of any air at C. Transfer the tube E to a large cylinder of water (see Fig. 18), let stand 30 minutes, adjust the tube so that the water both within and without the tube is at the same level, and read off the volume of gas. Take the temperature of the air, and ascertain the barometric pressure. The chemical changes may be expressed by the graph,



We have assurance that the chlorine combined with the magnesium, otherwise it would have been set free and have given to the water and the gas in E its characteristic odor. Whether the atoms reacted *in this proportion* it is the purpose of this experiment to determine.

The quantitative interpretation of these results may be divided into two essential phases.

1. "What is the weight of the hydrogen volume?"

It was pointed out on pages 40 and 41 that the volume of a gas varies directly with the temperature, and inversely with the pressure. In other words, its volume *increases with increased temperature*, and *decreases with increased pressure*. Therefore the same weight of magnesium would yield unequal volumes of hydrogen under different conditions of temperature and pressure. Scientists have agreed to accept 0°C. tempera-

ture, and 760 mm. pressure as their standard. It is commonly spoken of as *normal temperature and pressure*. The expression is usually abbreviated to N. T. P. The weight of 1,000 cc. of hydrogen at N. T. P. = 0.0896 gm. If we can ascertain what the volume of hydrogen obtained in the experiment will be at N. T. P., then we shall have a basis for determining its weight. Let us suppose that our volume, e.g., 59.4 cc., was read when the temperature was 14°C. and the barometric pressure was 750 mm.

It has already been pointed out that the volume of a gas varies directly with the temperature and inversely with the pressure. The volume of any gas at N. T. P. may be ascertained by the formula

$$V = \frac{V^1 P^1}{760 (1 + .00366T)}$$

(see Appendix), in which V^1 is the observed volume, P^1 the barometric pressure, and T the temperature. By substituting in this equation the values stated above we shall have,

$$V = \frac{59.4 \text{ cc.} \times 750}{760 (1 + .00366 \times 14^\circ)} = 55.8 \text{ cc., the vol. at N. T. P.}$$

How much will it weigh? The following proportion obtains:

$$1000 \text{ cc.} : 55.8 \text{ cc.} :: 0.0896 \text{ gm.} : X$$

$$X = .0049 \text{ gm.}$$

This is the weight of the hydrogen which was liberated by, e.g., 0.06 gm. of magnesium.

2. The second step in the process of finding how the atoms combined is comprehended in the question, "Do these weights represent some definite ratio?" Did one atom of magnesium react on one, two, or more molecules of hydrogen chloride? It was pointed out on page 51 that the gross weights of two substances are always in proportion to their respective individual weights, when the individuals composing these gross weights are 1 : 1.

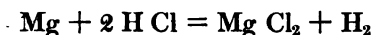
Were they in this proportion we should have,

At. Wt. H.	At. Wt. Mg.	Wt. of H.	Wt. of Mg.
------------	-------------	-----------	------------

1	:	24	::	.0049	:	.06
---	---	----	----	-------	---	-----

$1 \times .06 = 24 \times .0049$ from which we derive $.06 = .1176$.

This is *not* true; hence the hydrogen chloride and magnesium did *not* react 1 : 1. It is also apparent that the two products are in an approximate ratio of 2 : 1. If we substitute 2 for 1 in the above expression we shall establish an approximate proportion. This can only mean that two atoms of hydrogen were set free for each atom of magnesium contained in the .06 gm. of substance. We now rewrite the graph given on page 87,



It should be noted that no specific quantity of hydrogen chloride was used in this experiment. Doubtless thousands of molecules remained unchanged.

These results mean that a fixed quantity of the magnesium always yields a fixed quantity of hydrogen. In other words, it means that one atom of magnesium always liberates two atoms of hydrogen from its combination in an acid, i. e., *it always combines in a definite proportion.*

66. The Electrolysis of Water and Definite Proportions.—In Experiment 20 it was shown that the proportion of hydrogen to oxygen in a molecule of water is always 2 : 1. This is the definite or fixed proportion in which these atoms are combined in the molecule of water.

67. Composition of Ammonia, and Definite Proportions.—In Experiment 32, the graduated tube E was filled with a definite volume of chlorine. The ammonia solution in G was brought into the tube E in indefinite quantities; therefore the proportion in which the hydrogen and chlorine combined was

independent of the quantity of ammonia added. This means (1) that in ammonia the nitrogen and hydrogen are always combined in the ratio, 1 : 3; and (2) that in hydrogen chloride the two elements always combine in the ratio, 1 : 1, which ratio is *independent of any excess of either element.*

EXERCISES

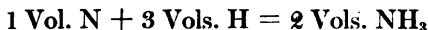
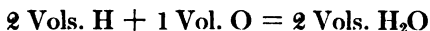
1. What will be the volume of 100 cc. of hydrogen, measured at 14° C. and 755 mm., when it is reduced to 0° C. and 760 mm.?
2. 1000 cc. hydrogen at N. T. P. weighs .0896 gm.; what would be the weight of 54.6 cc. measured under the same conditions?
3. What would be its volume when raised to 15° C. and 747 mm.?
4. How many gm. of hydrogen will be required to combine with 8.136 gm. of chlorine?
5. How many cc. at N. T. P. will this weight of hydrogen occupy, if two gm. at N. T. P. occupy 22.25 liters?
6. What will be the weight of 22.25 liters of chlorine measured at N. T. P.? Of oxygen? Of nitrogen?
7. How may the weight of *any* compound gas in 22.25 liters, at N. T. P., be calculated?
8. What would be the theoretical volume of 10 cc. (N. T. P.) of oxygen if it were cooled to -273° C.?

CHAPTER VI

FORMULAS AND 'MULTIPLE PROPORTIONS

It was shown in the preceding chapter that when two or more elements combine to produce a new substance the combination proceeds definitely, according to law. It will be the purpose of this chapter to discover this law and to apply it to the further interpretation of some of the preceding chemical expressions.

In the molecules of water, hydrogen chloride, and ammonia, the atoms always unite in a definite proportion by volume:



How do carbon, copper, silver, sodium, iron, etc., unite with other elements? Do they, too, obey the law of "definite proportions"? Since they are solids we cannot so conveniently study their behavior toward other elements by using this method of combination by volume; but, being matter, they have weight. Do they combine in definite proportions by weight? If so, what are the proportions? On page 49 it was shown that two parts by weight of hydrogen combine with 16 parts by weight of oxygen. Therefore, in the molecule of water the two elements are always combined in the weight ratio of 2 : 16. In Experiment 21 it was discovered that copper and oxygen were combined in the weight ratio of 63.57 : 16. Let us develop more data upon which to base a generalization of these weight ratios.

68. The Combination of Silver and Chlorine in Definite Proportions.—**EXPERIMENT 35.** Put about 1 gm. of pure silver (its symbol is Ag, [Argentum]), which has been accurately weighed, into a 300 cc. beaker, add about 10 cc. of nitric acid (1 : 5), heat the beaker on a water-bath until the silver is completely dissolved, and dilute it to exactly 300 cc.* Now the silver, which is an element, must have combined with all or a part of the nitric acid, whose molecular structure is at present undetermined. If this be represented by R, then we have the silver in combination as AgR. Put a measured quantity of this solution into a 300 cc. beaker, add about 10 cc. of hydrogen chloride, stir well with a glass rod, or a glass tube sealed at one end, cover the beaker, and let it stand in a dark place for about 24 hours, to insure a complete separation of the white curdy precipitate which forms when the two fluids are mixed. This precipitate should then be brought on to a weighed paper.† Suppose the final weight of bottle and paper = 30.086 gm. Adjust the weighed paper in a funnel of suitable size, place the weighing bottle in the desiccator for safe keeping, grease the under lip of the beaker with a little lard or tallow, filter off the precipitate, and bring every particle of it upon the paper. If the precipitate adheres to the sides of the beaker, rub the inside of the beaker thoroughly with a piece of rubber tubing fitted to the end of the stirring rod. When every particle of the precipitate has been removed, put the

*The solution may be equally divided among several students, thus economizing both time and material.

†It may be prepared as follows: Fold a filter paper 10 or 12 cm. in diameter, place it in a weighing bottle A, Fig. 27, heat the unstoppered bottle with its contents for two hours in a 100° drier (see Appendix), then stopper the bottle, place it in a desiccator until cool, and weigh it accurately. Unstopper the bottle, heat it again in the drier for an hour or two, let cool in desiccator, and weigh. Suppose the first weighing gave 30.1021 gm. while the second weighing gave 30.0860 gm.



FIGURE 27

This shows that 0.0161 gm. of water has been expelled. Continue heating as before until the last two weighings are the same, which means of course that the paper and bottle are free from moisture.

funnel with contents into the drier, and let it remain until apparently perfectly dry. Now remove the filter paper to the weighing bottle, taking great care not to tear the paper, and heat it in the drier as above directed until constant in weight, i. e., until all water has been expelled.

EXAMPLE. Suppose the final weight of bottle + paper + precipitate = 31.5110 gm. Let us interpret these results. When the silver was dissolved in nitric acid, a chemical change was produced, for the metal lost all of its former attributes. Since silver is an element, the process must have been synthetic. Therefore the metal combined with all or a part of the nitric acid producing AgR as noted above. The hydrogen chloride must have effected another chemical change. Otherwise no precipitate would have been formed. This means that the Ag did not remain in composition with R, and if not, it must have combined with Cl, H, or HCl. These possible combinations may be represented by the three graphs,

1. $\begin{array}{c} \text{AgR} \\ \vdots \\ \text{HCl} \end{array} = \text{AgH} + \text{RCl}, \text{ or some multiple thereof}$
2. $\begin{array}{c} \text{AgR} \\ \diagdown \\ \text{HCl} \end{array} = \text{AgHCl} + \text{R}, \text{ or some multiple thereof}$
3. $\begin{array}{c} \text{AgR} \\ \times \\ \text{HCl} \end{array} = \text{AgCl} + \text{HR}, \text{ or some multiple thereof}$

The actual course of the chemical action may be ascertained from the weights obtained. It should be borne in mind, however, that the weights in this illustration will differ in all prob-

ability from those obtained by the student. The following figures were taken from a student's note book:

Weight of silver used = 1.0700 gm.

" " bottle + paper + precipitate = 31.5110 gm.

" " " + " = 30.0860 "

1.4250 wt. of ppt.

Let us first determine the molecular weight of the compound. By employing the principle discussed in Experiment 21 we have,

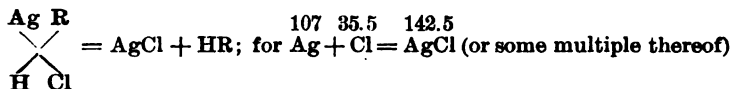
At. Wt. Ag		Mol. Wt. AgR		Wt. Ag		Wt. Solid
107	:	X	::	1.07 gm.	:	1.425 gm.
$1.07 X = 107 \times 1.425$						
$X = 142.5$, the molecular weight of AgR						

If we subtract the atomic weight of silver from the new molecular weight, 142.5, we have 35.5 as the weight of R, the unknown. Which of these hypothetical compounds approximates most closely in its molecular weight to 142.5? These approximations are shown in the following table:

						ERROR
In graph 1,	the molecular weight of	AgH	=	108	..	34.5
" " 2,	" " " " " "	AgHCl	=	143.5	..	1.5
" " 3,	" " " " " "	AgCl	=	142.5	..	0

This indicates that the third hypothesis is the correct one. We shall discover, in a subsequent chapter, that there are other reasons for believing that this is the true hypothesis. It remains to show that the precipitate contains both silver and chlorine: (a) Put one-half of it in a porcelain dish, add about 2 gm. of granulated zinc and 10 cc. of dilute sulphuric acid (compare Experiment 6), let the action continue fifteen or

twenty minutes, then add a little manganese dioxide to the mixture, heat it gently, and note the odor of escaping chlorine. (b) Mix the second portion with a little sodium carbonate and heat it very strongly on a piece of charcoal in the inner blow-pipe flame (p. 112). A bead of metallic silver will be obtained, which shows the presence of that element in the compound. Since both elements are present and the molecular weight is 142.5, it follows that the composition of the new molecule must be AgCl. We now have authority to write,



It is apparent from this graph that 107 parts by weight of silver combine with 35.5 parts by weight of chlorine and form 142.5 parts by weight of silver chloride.

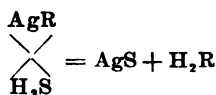
69. The Combination of Silver and Sulphur in Definite Proportions.—It will be helpful to study one other compound of silver. A solution of silver in nitric acid, saturated with hydrogen sulphide, gives a heavy black precipitate. After the precipitate has settled, the fluid should be filtered through a weighed paper, the precipitate dried, and weighed as directed for silver chloride in Experiment 35.

The following data were obtained by this process:

Weight of silver = 1.070 gm.

Weight of precipitate = 1.230 gm.

The qualitative reaction between the soluble silver compound and the hydrogen sulphide may be expressed by the hypothetical graph,



Now, if one atom of silver combined with one atom of sulphur, as assumed in the above graph, then by the principle announced in Experiment 21, we should have,

$$\begin{array}{rclclcl} \text{At. Wt. Ag} & & \text{Mol. Wt. AgS} & & \text{Wt. Ag} & & \text{Wt. of Solid} \\ 107 & : & 189 & :: & 1.07 \text{ gm.} & : & 1.23 \text{ gm.} \\ \text{and } 107 \times 1.23 \text{ should} & = & 189 \times 1.07; \text{ that is} & & & & \\ & & 181.61 \text{ should} & = & 148.73 & & \end{array}$$

Since this is not the case, it follows either that the experimental results are in error, or that the assumption is incorrect. Let us try another hypothesis, e. g., that two atoms of silver combined with one of sulphur; then we shall have,

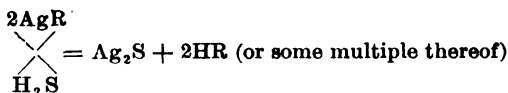
$$\begin{array}{rclclcl} \text{Mol. Wt. Ag}_2 & & \text{Mol. Wt. Ag}_2\text{S} & & \text{Wt. Ag} & & \text{Wt. of Solid} \\ 214 & : & 246 & :: & 1.07 \text{ gm.} & : & 1.23 \text{ gm.} \\ \text{and } 214 \times 1.23 \text{ should} & = & 246 \times 1.07; \text{ that is} & & & & \\ & & 263.22 = 263.23 & & & & \end{array}$$

This result seems to indicate that the second hypothesis is correct. It is very improbable that any other combination not expressed in the hypothesis would have given the same molecular weights. It remains only to show that the new compound contains both silver and sulphur.

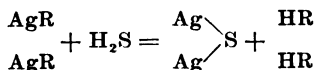
a. If one-half of the substance be placed in a porcelain dish, and about two gm. of granulated zinc and from 20 to 30 cc. of dilute sulphuric acid (1 : 3) added, the escaping gas has the characteristic odor of hydrogen sulphide.

b. If the second half is mixed with a little sodium carbonate, and heated on a piece of charcoal in the inner flame of the blow-pipe as directed in (II) page 112, a bead of silver will be obtained.

Since both silver and sulphur were present, and the molecular weight was 246, it follows that the composition of the new molecule must be Ag_2S . We now have the authority to write,



The numeral which precedes the molecule AgR denotes that two molecules of AgR react upon one molecule of H_2S . Thus,



Under these conditions the silver and sulphur atoms always combine in definite proportions by weight, 214 parts of silver to 32 parts of sulphur, yielding 246 parts of silver sulphide.

We now have the authority to prepare the following table of combinations:

TABLE II.

	FORMULA	COMB. BY WEIGHT
Hydrogen oxide	$\text{H}_2\text{O}, = 2\text{H} + \text{O}$	or 2 : 16
“ chloride	$\text{HCl}, = \text{H} + \text{Cl}$	“ 1 : 35.5
“ nitride	$\text{H}_3\text{N}, = 3\text{H} + \text{N}$	“ 3 : 14
“ sulphide	$\text{H}_2\text{S}, = 2\text{H} + \text{S}$	“ 2 : 32
Silver chloride	$\text{AgCl}, = \text{Ag} + \text{Cl}$	“ 107 : 35.5
Carbon dioxide	$\text{CO}_2, = \text{C} + 2\text{O}$	“ 12 : 32
Silver sulphide	$\text{Ag}_2\text{S}, = 2\text{Ag} + \text{S}$	“ 214 : 32

Observe that the name of each of these compounds ends in the suffix *ide*. Chemists have agreed that the names of all compounds which contain only two elements shall end in *ide* or *id*.

70. Combination in Definite Proportions.—A study of Table II shows that each element enters into the molecule in a proportion which may be expressed by its atomic weight, or some multiple of it. Thus, in the silver chloride molecule there are 107 parts by weight of silver, while in the silver sulphide molecule there are 214 parts. These numbers correspond respectively to the atomic weight, and to twice the atomic weight, of silver. In the first four formulas of the table, hydrogen enters the molecule in proportion to its weight, or twice or three times that weight. In the experimental examination of a large variety of compounds it has been found *that the gross weight of any element in any given compound is always in proportion to the atomic weight of that element, or to some multiple of that atomic weight.*

7.9 gm.	of CuO	contain	6.3 gm.	of Cu	and	1.6 gm.	of O
246 “	“ Ag_2S	“	214 “	“ Ag	“	32 “	“ S
170 “	“ NH_3	“	140 “	“ N	“	30 “	“ H
180 “	“ H_2O	“	160 “	“ O	“	20 “	“ H

71. Elements Combine in Definite and Multiple Proportions.—The above law of combination by weight, called the law of multiple proportions, leads to the belief that all atoms of a given element have exactly the same properties, that they are mutually interchangeable, and, most significant of all, that they cannot be divided. The following consideration will make this point clear: Suppose a large pile of shot is made up of individual shot each one of which weighs exactly 1 gm. Then the weight of any quantity of shot will be expressed by a whole number. Let the reasoning be reversed. Suppose it is found that in every case the *gross weight* of any given quantity of shot is a whole number. The gross weight is made up of individual weights, and each of these must be a whole number. The discovery of this law of "multiple proportions" led Dalton to his theory that all compounds are made up of atoms. His generalization was based upon a few facts only, but all results obtained since his time confirm the law. This law of multiple proportions is fundamental in chemical science, for a great variety of phenomena are explainable only in terms of it. One of its numerous applications is the explanation of *valence*.

72. Multiple Proportions and Valence.—Valence includes (1) the *power* which atoms have to combine with others, and (2) the *proportions* in which the combining atoms unite.

I. The power which atoms have to combine and form new substances is spoken of as their *affinity*. In determining the formula for hydrogen chloride (p. 58), we found that the chlorine combines with the hydrogen with great ease. It is said, therefore, to possess a great affinity for that element. It was shown in Experiment 28 that nitrogen will not burn in oxygen, which is only another way of saying that these elements do not possess a strong affinity for each other.

This term "affinity," then, expresses a theory of atomic attraction.

II. The *proportions* in which atoms enter into combination with other atoms is sometimes spoken of as the *combining power*. Some atom must be selected as a standard, in terms of which this power may be measured. This is not difficult. In HCl we have a molecule which contains two atoms. If we accept the combining power of an atom of chlorine as one, then that of an atom of hydrogen must also be one; therefore the combining power of either may be spoken of as the standard or unity. If the combining power of H = 1, that of Cl and that of Ag (see p. 95) is also one. Since one atom of oxygen combines with two atoms of hydrogen, the oxygen atom must be equivalent to two hydrogen atoms in its combining power. In the ammonia molecule we have three atoms of hydrogen combined with one atom of nitrogen. It follows that the nitrogen atom possesses three times the combining power of the atom of hydrogen. It was pointed out on page 80 that one atom of carbon combines with two atoms of oxygen to form carbon dioxide. What then is the combining power of a carbon atom? The combining power of two atoms of oxygen must be four times that of one atom of hydrogen, and since one atom of carbon holds these two atoms of oxygen whose power is four, it must have a combining power of four. An atom of carbon is said, therefore, to possess *four hydrogen equivalents*. In water, oxygen is shown to possess two hydrogen equivalents, while nitrogen in ammonia shows three. *The power of one atom to hold other atoms in combination, expressed in hydrogen equivalents, is called its valence.*

The following table of valences may be arranged from the formulas tabulated on page 97:

H, Cl, and Ag = 1; O and S = 2; N = 3; C = 4

For convenience, the valence of atoms may be represented

graphically by dots or lines. It should be borne in mind, however, that this is only a device to enable the student to image more readily the arrangement of the atoms in the molecule. Representing each atom by a sphere, we have,

Hydrogen (H),	valence 1,	may be represented thus	●
Oxygen (O)	" 2,	" " " "	●—●
Nitrogen (N)	" 3,	" " " "	●— ●
Carbon (C)	" 4,	" " " "	●— ●— ●

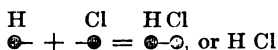
An atom whose valence is 1 is called a monad, and is said to be univalent; one whose valence is twice that of chlorine or hydrogen is called a diad, and is said to be bivalent; those whose valence is 3, 4, 5, and 6 are named respectively triads, tetrads, pentads, and hexads. They are spoken of respectively as trivalent, quadrivalent, quinquivalent, or sexivalent.

EXAMPLE.—

H,	valence 1,	is a monad,	and is univalent in action.
O,	" 2,	" " diad	" " bivalent " "
N,	" 3,	" " triad	" " trivalent " "
C,	" 4,	" " tetrad	" " quadrivalent " "
P,	" 5,	" " pentad	" " quinquivalent " "
S,	" 6,	" " hexad	" " sexivalent " "

73. Valence and the Structure of Molecules.—The graph may also serve to represent the *structure* of a molecule. In using it for such a purpose it should be borne in mind that unit valence of one atom always unites itself with unit valence of another atom.

EXAMPLE.—



When a straight line is drawn between two atoms, it signifies that two such unit valences have united. This statement will

serve to explain more fully the graph for the molecule of ammonia used on page 73.

74. Variation in Valence.—Valence is more difficult to understand than would appear from the foregoing discussion, because it is not fixed, but varies according to conditions. An element may combine with another element in more than one proportion, as illustrated in the following:

Reduction of Carbon Dioxide to Carbon Monoxide.—We have examined somewhat in detail the properties and structure of carbon dioxide. Its density, 22, and the method used in its synthesis, show that the molecule contains one atom of carbon and two of oxygen, and that its formula is CO_2 . It is possible to withdraw one atom of oxygen from this molecule, thereby reducing it to carbon monoxide, CO . This reduction usually takes place when carbon dioxide is passed over red-hot charcoal. The reaction may be expressed by the graph,



Carbon monoxide is formed whenever carbon is burned with an insufficient supply of oxygen. This usually occurs when the draught of a furnace or stove is not strong enough to promptly remove the carbon dioxide and other products of the combustion. The pale blue flame which may be observed above a bed of live coals is due to the combustion of carbon monoxide.

Carbon monoxide is a strong poison to all warm-blooded animals, for it combines with one of the compounds in the blood in such a way that the blood cannot carry oxygen to the various tissues. It is especially dangerous because its effects are not immediately recognized. An animal inhaling air containing one per cent or more of this gas passes into a stupor from which it seldom recovers. Stoves of imperfect construction give it off into the surrounding air, which quickly becomes unwholesome unless there is free and copious ventilation.

This brief study teaches us that valence is not an *absolute* property of an atom, like its atomic weight, which is constant under all conditions. It seems to be rather an expression of the mutual action of two or more elements.

The data developed in this chapter establish three very important characteristics of all atoms:

a. Atoms always enter into combination either in proportion to their atomic weight or some multiple of it.

b. This proportion is determined by the acting valence of the participating elements.

c. Atoms always unite in such a proportion that the valences of all the participating elements are satisfied. This third characteristic may be verified by examining the formulas on page 97.

75. Valence and Compounds.—These three characteristics of atoms determine the composition of any substance. Some of the preceding graphs may now be interpreted in terms of these facts.

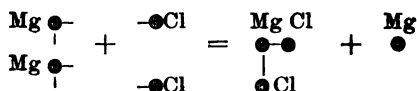
It was pointed out on page 51 that the gross weights of two elements must be proportional to the respective atomic weights in order that these elements may be in the ratio of 1 : 1.

EXAMPLE.—If we wish to weigh out magnesium and chlorine so that the atoms shall be equal in number, that is, 1 : 1, then the weights must be proportional to the atomic weights.

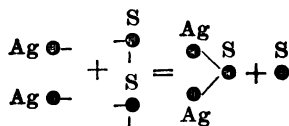
At. Wt. Mg	At. Wt. Cl	Wt. Mg	Wt. Cl
24	: 35.5	: : 1.2 gm.	: 1.77 gm.

What would be the result if the two elements brought together in this proportion were caused to combine? Would the product be MgCl ? It was established in Experiment 34 that one atom of magnesium combines with two atoms of chlorine to form magnesium chloride, MgCl_2 . It must be apparent that

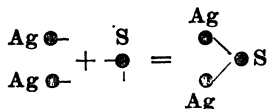
unless the magnesium atom alters its customary valence to suit the new conditions (valence is not constant), half of it will not be acted upon. Thus,



76. Valence and Equivalent Quantities.—Suppose we weigh out 1.07 gm. of silver and 0.32 gm. of sulphur and unite the two by appropriate methods, what compound will result? It was established on page 96 that two atoms of silver combine with one atom of sulphur. Therefore, unless the silver or sulphur alters its customary valence to suit the new conditions, we shall have,



One-half of the sulphur will remain inactive. In order that all of the sulphur may participate in the reaction, the ratio of the atoms of the respective elements must be 2 : 1. How could this ratio be maintained in weighing the gross quantities? If a proportion of 107 : 32 always gives an equal number of atoms of these elements, then a proportion of 107 : 16 would give twice as many atoms of silver as of sulphur. This is the proportion in which the two elements combine:



One hundred seven is the atomic weight of silver, and 16 is one-half the atomic weight of sulphur. The sulphur

atom has been brought to equivalence with a monad, by using one-half the number of atoms. This is technically known as "one hydrogen equivalent." *The hydrogen equivalent of any element is its atomic weight divided by its valence.* This proportion is usually spoken of as the "equivalent quantity." A general expression for equivalent quantities may be deduced.

Let A and B represent two elements whose hydrogen equivalents are wanted.

M = atomic weight of element A, and V its valence

M' = " " " " B, " V' " "

W = gross weight of element A

W' = " " " " B

$$\text{then} \quad (1) \quad \frac{M}{V} : \frac{M'}{V'} :: W : W' \quad (2) \quad \frac{MW'}{V} = \frac{M'W}{V'}$$

$$(3) \quad W' = \frac{M'WV}{V'M} \quad (4) \quad W = \frac{MW'V'}{VM'}$$

EXAMPLE.—1. How many gm. of oxygen will be required to combine with 0.4 gm. of silver?

	VALENCE	ATOMIC WEIGHT
Let M = Ag.....	1	107
M' = O.....	2	16

By substitution in (3) we have,

$$W' = \frac{16 \times 0.4 \times 1}{2 \times 107} = .029 \text{ gm. of oxygen}$$

2. How many gm. of silver would be required to combine with 0.4 gm. of oxygen?

By substitution in (4) we have,

$$W = \frac{107 \times 0.4 \times 2}{16 \times 1} = 5.35 \text{ gm.}$$

Summary.—The data of the preceding chapters establish the following fundamental principles:

1. The atomic theory of matter is a reasonable working hypothesis.

2. With very few exceptions the density of a compound in the gaseous state is one-half of its molecular weight.

$$D = \frac{\text{Mol. Wt.}}{2}$$

3. Atoms always combine in definite proportions.

4. These proportions by weights vary directly as the atomic weights of the atoms, or of some multiple thereof.

5. The proportions in which an atom enters into combination with another atom or atoms is a measure of its valence.

6. The valence of an atom may vary (a) with the temperature at which combination occurs, and (b) according to the variety of elements with which it combines.

7. The gross weights of two elements will possess equal combining power when they are proportional to the quotients obtained by dividing the atomic weights of these elements by their respective valences. Each is said to have been brought to the basis of "one hydrogen equivalent." This relation is expressed in the general formula,

$$\frac{MW}{V} = \frac{M'W'}{V'}$$

where M is the molecular weight and V the valence of one element (A); and M' is the molecular weight and V' the valence of another element (B).

EXERCISES

1. It is found that 200 cc. nitrogen combine with 300 cc. oxygen, forming 200 cc. of a new gas. Determine its formula.

2. 107 gm. of silver combined with 127 gm. of iodine. What is the ratio of the atoms in the molecule of the compound?

3. Suppose Dalton had discovered a new compound of silver and iodine which contained 107 parts by weight of silver and 190.5 parts

by weight of iodine. What influence would it have had on his law of multiple proportions?

4. What relation does Dalton's law bear to valence? Is valence an absolute property of atoms?

5. How many gm. of oxygen will be required to burn 13 gm. of carbon to carbon dioxide?

6. In what proportions by weight must silver and sulphur be mixed, that the two quantities shall be chemically equivalent?

7. What weights of any series of elementary substances must be taken so that the atoms will be in the ratio of 1 : 1?

8. Would .63 gm. of copper and .32 gm. of sulphur give an atomic ratio of 1 : 1?

9. Would these two quantities be chemically equivalent in their combining power?

CHAPTER VII

THE RELATION OF VALENCE AND MULTIPLE PROPORTIONS TO OXIDATION AND REDUCTION

In the descriptive matter of the preceding pages we have used two terms to which we need to give more specific meaning:

- (a) Combustion, or oxidation, and
- (b) Reduction or deoxidation.

77. Oxidation.—In the synthesis of H_2O , CuO , and CO_2 it was shown that the oxygen combined with these three elements to form oxides. In the formation of water and carbon dioxide, the chemical union was made manifest through the evolution of light and heat. We know from the weights given on page 49 that the absorption of oxygen by copper was also an oxidizing process. The term “combustion” is popularly associated with those oxidizing processes in which light and heat are evolved, such as the burning of wood, coal, oil, tallow, and most other compounds of carbon. Combustion, in its scientific significance, is a broader term than oxidation. In Experiment 23 it was shown that sodium burns with a brilliant yellow light in chlorine, yielding sodium chloride. In Experiment 25 the hydrogen flame continued to burn in chlorine, producing hydrogen chloride. Both are cases of true combustion, but not of oxidation.

I. Stahl's Theory: Phlogiston.—In 1697, Stahl advanced the “phlogiston” theory of combustion. This theory assumed the existence of a mysterious substance which the author called “phlogiston,” and that combustion was the escape of this substance from the burning body. According to this theory, when

two sticks are rubbed together rapidly and forcibly, the wood ignites because phlogiston is disengaged from it. This theory was for a time very generally accepted.

II. *Theory of Lavoisier.*—Stahl's view of combustion was completely changed by Lavoisier, in 1774, when he announced the theory that combustion is due to the combination of oxygen with other elements. His theory was based upon the following celebrated experiment:

A retort A, Fig. 28, with a long curved neck reached well up into a cylinder C. This cylinder was inverted over a bath

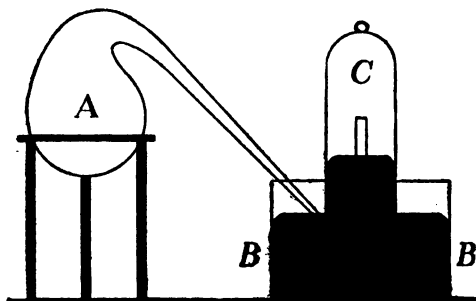


FIGURE 28

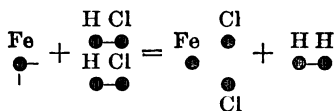
of mercury B B. Lavoisier placed a weighed quantity of mercury in A, connected the apparatus as shown in the cut, accurately measured the volume of air in A C, and then heated the receiver A nearly to the boiling point

of the mercury for several days. By this means the mercury absorbed the oxygen contained in A and C, forming, as we now know, mercuric oxide. The heat was sustained until a decrease in the volume of air was no longer perceptible. The residual volume was four-fifths of the original, showing that one-fifth of it had combined with the mercury. The chemist ignited the mercuric oxide and obtained a quantity of gas equal in volume to that which had been withdrawn from the air, and by mixing this with the residual nitrogen in C, the original volume and attributes of air were restored. He thus proved that air is a mixture of about four volumes of nitrogen and one volume of oxygen.

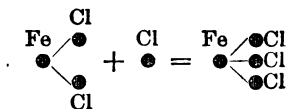
Out of this experiment came a second and more important

deduction. Lavoisier found that the increase in the weight of the mercury when the oxygen was united with it, was exactly equivalent to the loss in weight of the mercury when the combined oxygen was restored to the air by ignition. He thus demonstrated that the process of oxidation is the union of two elements, and that the weight of the product is equal to the combined weights of the elements. All subsequent investigations have sustained this view. This experiment is important because it gave a really scientific impulse to chemistry.

78. The Relation of Oxidation to Valence.—At present the term oxidation is sometimes used in a special sense; an element is said to be oxidized when it is made to act with *increased* valence. Thus, an atom of iron may combine with the two atoms of chlorine in hydrogen chloride, to form a molecule of iron dichloride.



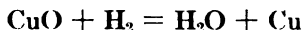
When chlorine comes into contact with this molecule, it effects a peculiar change. The substance loses its former attributes and becomes a new individual. The change in the molecule may be shown by the graph,



The atom of iron has *increased* its *valence* from two to three. It is said to have been oxidized, but it is apparent that no oxygen has been absorbed. Hence an oxidizing agent is one which has the power either to liberate oxygen, or to increase the valence of an element. The most important of the ordi-

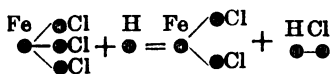
nary oxidizing agents in use in the laboratory are chlorine, bromine, oxygen, nitric acid, potassium chlorate, chromic acid, potassium nitrate, ammonium nitrate, and the oxidizing zone of the bunsen flame.

79. Reduction.—It will now be of advantage to inquire into the meaning of reduction. Experiment 21 illustrates the use of this term. It was pointed out there that the hydrogen combined with the oxygen in copper oxide to form water and pure copper. This may be expressed by the graph,



Here the oxygen has been withdrawn from the copper oxide, and the latter is said to have been *reduced*. The graph also shows that the hydrogen, which was the agent of reduction, was itself oxidized. Reduction here consists in the withdrawal of oxygen from a compound.

80. The Relation of Reduction to Valence.—Modern chemistry has given to the word reduction another and larger significance. In its broadest sense it means *decrease* in the *valence* of an atom or a combination of atoms. Oxidation in valence may be independent of oxygen, for it was pointed out on page 109 that iron dichloride can be oxidized to iron trichloride by chlorine. The process may be reversed; the iron trichloride may be reduced to iron dichloride after the following graph,



Therefore a reducing agent is one which has the power to withdraw oxygen from a compound or to *decrease* the acting valence of an element, or a group of elements. The most important of the ordinary reducing agents used in the

laboratory are hydrogen, carbon, nitrogen sulphide, and the reducing zone of the bunsen flame.

81. The Gas Flame as an Oxidizing and a Reducing Agent.—I. *The bunsen burner*, Fig. 29, consists of a central barrel B, which is provided with a window C, which may be closed by an adjustable collar C'. These two features enable the student to control the supply of air which reaches the inside of the flame. When C is opened and the gas is ignited at D, it is observed to burn with a very pale blue flame. When C is closed the flame becomes much more luminous, yellow, and smoky. When the window C is open, the flame will be observed to consist of three zones, two of which are especially distinct—an inner hollow one, E, and an outer solid one, G. That the inner zone E is hollow may be shown by holding the shaft of a match in and across the flame. Two parts of the match, coinciding with the outer edges of the flame, will be charred, while the intervening space is unchanged. That the zone G contains no such hollow space may also be shown with the match. What do these zones signify? The gas which enters at A is a compound of carbon and hydrogen, principally CH_4 . It fills the barrel of the lamp, and when C is open, reaches the upper part D, already mixed with some air. Here it is surrounded by an outer layer of air which, with the inner air supply, is sufficient to oxidize the gas completely. This process may be expressed by the graph,

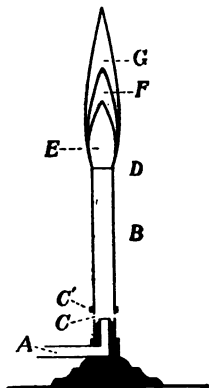
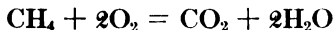


FIGURE 29



Both products are gases and are therefore dissipated into the surrounding air. Now air is viscous, and while the gas is

burning there will be a strong upward current, which, because of this viscosity, will draw a comparatively large quantity of air after it. The zone G will in consequence be rich in oxygen. The zone E is much poorer in oxygen, and if the window C be closed, will be practically free from it. Suppose a small quantity of copper oxide is placed in the apex of the reducing zone F. The gas CH_4 within this zone combines with oxygen according to the graph above. It follows that the copper oxide will be reduced to metallic copper, while the CH_4 will be oxidized to CO_2 and $2\text{H}_2\text{O}$ by the oxygen withdrawn from the copper oxide;



This reducing power may be increased by heating the copper oxide on charcoal in the inner blow-pipe flame.

II. *The Blow-pipe*.—The blow-pipe A, Fig. 30, is a device for obtaining a horizontal flame. Its flame, Fig. 31, possesses an oxidizing zone D, and a reducing zone B. It is similar to the colorless bunsen flame in that the air is blown into the middle of the combustible gases. The hottest part of this flame is where the dark inner zone, B, terminates in a bluish vertex, C. When copper oxide is placed on the charcoal E and exposed to the inner blow-pipe flame,

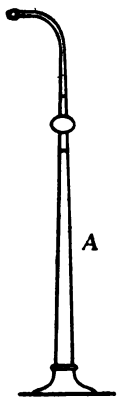


FIGURE 30

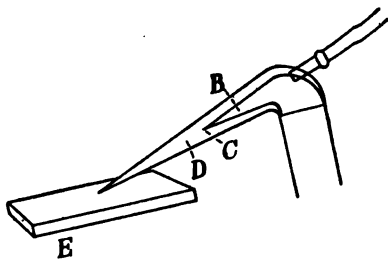


FIGURE 31

flame, the combined action of the hot charcoal and the gas within this zone readily reduces it to metallic copper.

III. *Candle and Lamp Flames*.—The brightness of a flame depends upon:

1. The degree of heat, and
2. The presence of solid particles.

A flame which contains no solid particles emits a feeble light regardless of the temperature; but when solid particles are present, the brightness increases with the temperature. Any substance which burns with such energy that the temperature of the flame becomes very high, will produce a light of great intensity if the product of the combustion is a solid. This fact is illustrated by the burning of phosphorus and magnesium in the air, and the combustion of iron in oxygen.

When there is incomplete combustion of any carbon compound, solid particles of free carbon separate and become incandescent. This is the case in a candle or coal-gas flame.

The candle flame, Fig. 32, consists of a dark inner zone A, which is made up of combustible gases coming through the wick from the melted tallow or wax, some nitrogen, and products of combustion, viz., water and carbon dioxide. The blue zone B is highly luminous because the supply of air does not penetrate far enough into the flame to oxidize the carbon completely. The outer zone C is practically non-luminous because the combustible gases which reach it are there completely burned.

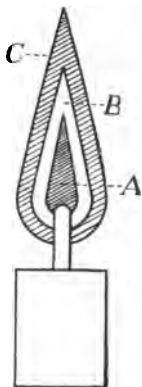


FIGURE 32

82. Oxidation and Reduction in the Preparation of Iron and Steel.—Oxidation and reduction are of immense importance in their practical applications. The utilization of the reducing process is well illustrated in the preparation of commercial iron and steel. The manufacture of commercial iron consists essentially in the reduction of its oxides, such as hematite, Fe_2O_3 ; magnetite, or loadstone, Fe_3O_4 ; and limonite

2FeO_3 , $3\text{H}_2\text{O}$. These three are the ores chiefly used by manufacturers of iron and steel. Their reduction is usually effected

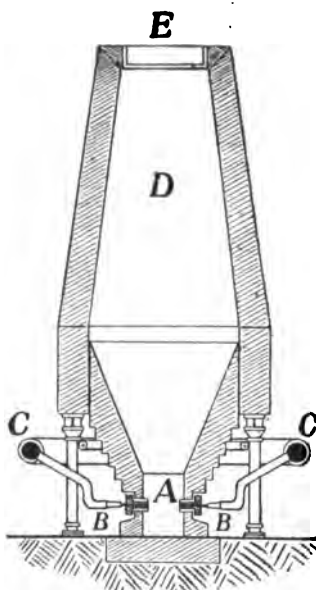


FIGURE 33

in blast furnaces which vary in size and shape. The size depends largely upon the kind of fuel to be used, a coke-fed furnace being larger than one which is fired with soft coal. Experience has shown that the best results are obtained from a furnace about 75 ft. high, with a capacity of about 12,000 cu. ft. Externally (Fig. 33) the furnace is somewhat cylindrical, while internally it is like the frustra of two hollow cones placed base to base. It is lined with the most refractory variety of fire brick. Such a furnace, adapted for reducing hematite ore, is shown in the cut. It consists essentially of the central shaft D, into which the fuel and ore are put, a contracted portion A, called the crucible, which serves to collect the

molten iron, and pipes B B, which open into A from the large pipe C. These pipes, B B, are used to conduct into the upper portion of the crucible a blast of hot air, supplied by forcing air through large cylindrical steel stacks, which are kept hot, into the pipe C, from which it is distributed to the pipes B B, called tuyeres (pronounced twee-ers).

I. Preparation of Pig Iron.—The fundamental procedure is as follows: The initial fire is started in the crucible A in the usual way. When this is thoroughly heated, a heavy charge of fuel is introduced through the opening at E. A layer of ore is then introduced, then alternate layers of fuel and ore, until the large stack is sufficiently full. The opening at E is closed,

and the hot air blast is turned into the crucible A through the tuyeres B B. The combustion is so intense in the crucible that a zone of very high heat is produced. The combustion, which of course takes place simultaneously in the other portions of the stack, decreases in intensity from the crucible to the top. The distribution of the resulting zones of temperature is shown in Fig. 34. These figures, by Lowthian Bell, were obtained

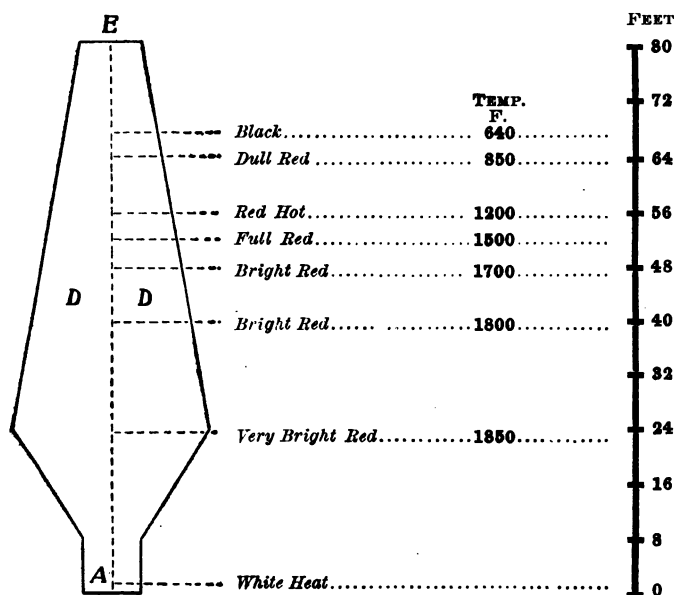
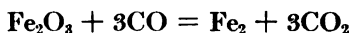


FIGURE 34

by taking the temperature from holes at convenient heights drilled through the walls of the stack. The chemical changes which take place are essentially reduction and oxidation, the reduction of the iron oxide to metallic iron, and the oxidation of the carbon to carbon dioxide. The nearly complete combustion of the carbon in the crucible produces metallic iron, carbon dioxide, and carbon monoxide.



The gases pass up through the strata of hot carbon and ore, where the carbon dioxide is largely reduced to carbon monoxide. The carbon monoxide is combustible, uniting with oxygen to form carbon dioxide. It is therefore a reducing agent. Since the oxygen from the tuyeres has been largely combined in the crucible, the carbon monoxide must draw its oxygen from the ore. It is consequently active in reducing the iron to the metallic state. This process may be expressed by the graph



The metallic iron is gradually melted and collected in the crucible, from which it is periodically run off into casting beds made of sand, where it is moulded into sticks or blocks.

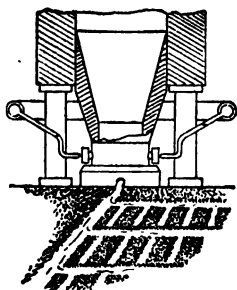


FIGURE 35

These are known commercially as "pig" (see Fig. 35), or "cast" iron. The molten iron in the crucible may be transferred directly to the "converter" and manufactured into steel.

II. *The Transformation of Pig Iron into Steel.*—This pig or cast iron may be regarded as the raw material from which steel is made. Chemically, cast iron differs from steel in the quantity of carbon which it contains. When the oxide is first reduced to metallic iron, it is in a very pure state. As it descends through the glowing carbon it takes up some of the carbon. This process is both mechanical and chemical, and the ratio of the mechanically mixed to the chemically combined carbon in the iron, gives rise to two varieties of iron, white and gray. The white variety contains about two per cent of carbon, which is largely in chemical union with the iron. This form is silver-white, very hard, always crystalline, and quite brittle. Gray cast iron is softer and closer-grained than the white, and contains more carbon.

The white variety is the one chiefly used in the manufacture of steel and wrought iron. Steel and wrought iron differ chemically in the quantity of carbon which they contain. Steel contains from 0.6 to 1.5 per cent, while wrought iron has only from 0.15 to 0.3 per cent.

Wrought (or malleable) iron has a clear gray color and a specific gravity of 7.7–7.8. It is softer than cast iron or steel, and may be drawn into the finest wire or hammered into very thin sheets. When two pieces are heated to redness, placed in contact and vigorously hammered, they unite so intimately as to form practically one piece, and are said to have been welded.

The quality of iron is greatly influenced by the presence of phosphorus and sulphur. Even .01 per cent of phosphorus renders the iron brittle when cold, and an equally small quantity of sulphur will make it brittle when hot, so that instead of welding into a close joint under the hammer, it splits and crumbles. The problem of the manufacturer is to remove these two objectionable elements.

Steel is of a gray-white color and of a finely crystalline structure, with a specific gravity of 7.6–7.8. The hardness may be increased by heating to redness and plunging into cold water. This acquired hardness or “temper” may be removed by annealing, i. e., reheating and allowing to cool very slowly. Steel partakes, therefore, of the properties of both cast and wrought iron.

Steel may be made in two ways: One way is by increasing the carbon in wrought iron to between .6 and 1.5 per cent, either (a) by adding carbon directly to it, or (b) by adding pig iron until the carbon is sufficiently increased. Another way is to remove the excess of carbon from the pig iron.

Of these two methods the former is the older and in some respects the better. It was the custom to put the bars of wrought iron into boxes of fire-clay, bed them in charcoal,

close the boxes to exclude all air, and heat the contents to redness for a week or ten days, after which they were allowed to cool slowly, when the bars were found to be brittle, covered with peculiar blisters, and readily fusible. They were then placed in crucibles of fire-clay or graphite, a little powdered manganese dioxide added, the mixture fused and cast into ingots. These ingots were afterwards heated and drawn out into bars. This was known as "cast steel." The whole process is known as cementation, and "cementation steel" is still considered the best for fine cutlery, etc. The most serious objection to the process is the time consumed for each casting. Bessemer, in about 1856, invented a quicker process known as the "Bessemer process." It consists of two stages:

1. The removal of the carbon from pig iron, and
2. The addition of enough pig iron to bring the per cent of carbon up to from 0.6 to 1.5 per cent.

The first stage is effected through the use of a Bessemer

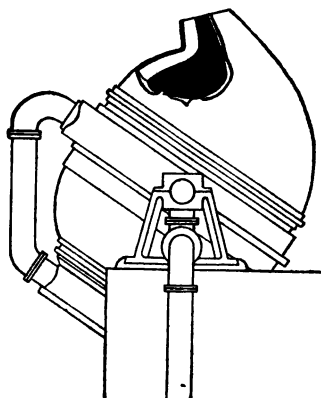


FIGURE 36

converter, shown in Fig. 36. It is made of wrought iron and lined with an infusible material. Five or six tons of molten pig iron are poured into it and a blast of air, under powerful pressure, is forced up through the iron. The combustion of the carbon in the iron furnishes all the heat necessary. The temperature is raised to about $2,000^{\circ}$, and the heat is maintained until the per cent of carbon falls below 0.6. This is ascertained by ob-

serving the color or the spectrum of the flame which issues from the mouth of the converter. A sufficient quantity of melted pig iron is then added to bring the per cent of carbon

in the whole up to the required standard. The steel is then poured into molds and allowed to cool. These are the "steel billets" of commerce.

The real function of the converter is made clear by the following series of analyses, by Mr. Snelus,* of the escaping gases taken at different intervals during the blow.

TABLE III

I. Changes in the proportion of gaseous contents of the converter:

TIME AFTER STARTING	2 MIN.	4 MIN.	6 MIN.	10 MIN.	12 MIN.	14 MIN.
Free oxygen.....	0.02					
Carbon dioxide.....	10.71	8.59	8.20	3.58	2.30	1.34
Carbon monoxide....		3.95	4.52	19.59	29.30	31.11
Hydrogen.....		0.88	2.00	2 00	2.16	2.00
Nitrogen.....	88.37	86.58	85.28	74.83	66.24	66.55

TABLE IV

II. The solid contents of the converter undergo the following changes:

PIG IRON		FIRST PERIOD	SECOND PERIOD	THIRD PERIOD
Graphite.....	3.18			
Combined carbon.....	0.75	2.465	0.949	0.087
Silicon.....	1.96	0.443	0.112	0.028
Sulphur.....	0.018	trace	trace	trace
Phosphorus.....	0.04	0.04	0.045	0.045
Copper.....	0.085	0.091	0.095	0.120
Manganese.....	3.46	1.645	0.429	0.113

The product in the last column is the one to which the calculated quantity of pig iron is added in order to raise the carbon from 0.6 to 1.5 per cent.

The invention of Bessemer practically revolutionized the manufacture of steel. Now ten tons of crude cast iron may be transformed into good steel in less than thirty minutes in a

* See Bell's "Principles of the Manufacture of Iron and Steel."

single converter. Steel prepared in this way is extensively used in rails, bridges, and boilers.

The injurious phosphorus may be removed by the "Thomas Gilchrist" modification of the Bessemer process. In this modification, the converter is lined with a variety of limestone known as dolomite. A certain quantity of lime is added to the molten mass, and the carbon is blown out as above described. Practically all of the phosphorus is taken up by the lime and the lining of the converter. The lime in combination separates from the steel as a scum or slag. It is apparent that the fundamental chemical processes in the manufacture of iron and steel are oxidation and reduction.

83. Preparation of Wrought Iron.—Wrought iron was first made by a process known as puddling. The furnace in

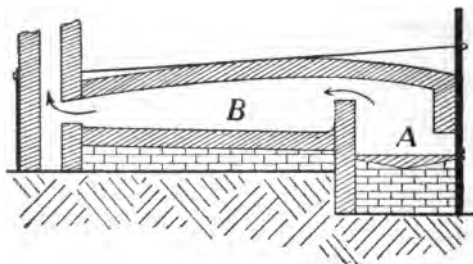


FIGURE 37

which this was effected has a flat hearth and a low-arched roof, as shown in Fig. 37. The sides and roof are lined with hematite or some other iron ore. The oven B is charged with pig iron, which is then exposed to an intense heat from the coal or gas fire in A. The iron is melted and the carbon is gradually removed from it, partly by the oxygen of the air, but chiefly by that of the ore with which the furnace is lined. During the process the molten metal is constantly stirred or shaken until it becomes pasty. The spongy mass is then

rolled, or beaten with a trip hammer. By this process the slag is squeezed out. This greatly improves the product. The chemistry of this process is reduction similar to that occurring in the manufacture of the pig iron.

EXERCISES

1. Define oxidation and name two oxidizing agents.
2. Define reduction and name two reducing agents.
3. Why does burning magnesium give so brilliant a light?
4. Would burning calcium or barium give a very luminous flame?
Why?
5. Why is a candle-flame not colorless?
6. What would be the effect upon a lamp-flame, if carbon dioxide were a non-volatile solid?
7. Should the top of a blast-furnace be open or closed during the reduction of a charge of ore?
8. Do blacksmiths weld cast iron? Why?
9. Why are nails made of steel instead of wrought iron?
10. What kind of iron is used in building bridges? Why?
11. Would iron which contains 2 per cent of carbon be suitable for making car wheels? Why?
12. How many tons of fuel are required to make one ton of Bessemer steel from pig iron?

CHAPTER VIII

BASES AND ACIDS

It will now be our purpose to study the action of oxidation and reduction in building up two important classes of compounds, bases and acids. The elements sulphur and phosphorus will serve for this study.

SULPHUR, S (AT. WT. 32.06)

84. This familiar substance, regarded by the alchemists as a peculiar combination of phlogiston with some unknown acid, was proven by Lavoisier to be an element. Sulphur is found free, deposited in crystals, lumps, or thin sheets, in the vicinity of extinct and active volcanoes. Such deposits are found in Italy, Sicily, Spain, Roumania, California, Mexico, South America, Nevada, Utah, Yellowstone Park, etc. Sulphur issues from many volcanoes as a vapor, which solidifies and crystallizes on cooling. Much of the sulphur of commerce is obtained from Italy and Sicily, which yield annually about 85,000 tons. In combination with a metal it occurs in the sulphides of copper, lead, zinc, mercury, iron, and other minerals of wide distribution. Sulphur forms an essential part of animal albumen, and is found to some extent in vegetable tissue. The peculiar properties of mustard and garlic are due to compounds of sulphur.

85. Preparation of Sulphur.—The method of preparing sulphur consists in melting the native product and allowing the liquid to drain off from the dirt with which it is mixed, after which the liquid is allowed to solidify. The crude product is

put into a receiver A, Fig. 38, where it is melted by the surplus heat from the fire D. It then runs through the tube B into the chamber C, which is sufficiently heated to vaporize it. The vapor enters a large brick chamber E, and is there con-

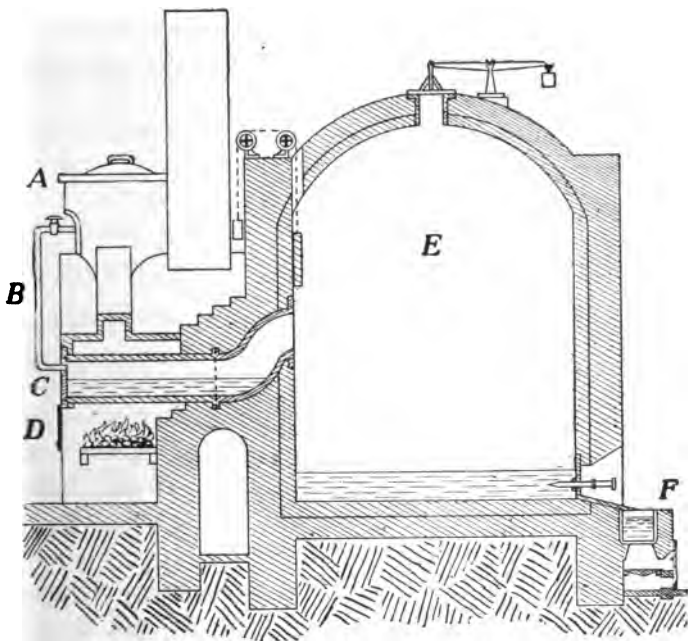


FIGURE 38

densed. The first product is a very fine powder known in commerce as "flowers of sulphur"; but when the walls become hot, the vapor condenses to a liquid, which collects on the floor and is drawn off into the receiver F and moulded into what is called "roll brimstone."

86. Properties and Uses of Sulphur.—Sulphur is a lemon-yellow substance, brittle at ordinary temperature, and insoluble in water. It is extensively used in the manufacture

of gunpowder, sulphuric acid, vulcanized rubber, and certain kinds of matches, and in bleaching silk and woollen goods.

87. Allotropic Forms of Sulphur.—Sulphur is met with in trade both in the crystalline and the amorphous condition. The native crystals are yellow, more or less transparent rhombic octahedra, shown in Fig. 39, A. The same type of crystal may be prepared in the laboratory by dissolving a quantity of the powdered sulphur in carbon bisulphide, and allowing the solution to evaporate slowly. Crystals so prepared have, like the native crystals, a specific gravity of 2.05–2.07 (water = 1), and melt at 114.5° C.

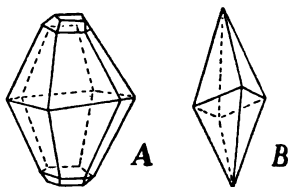


FIGURE 39

If these crystals are melted and the liquid allowed to cool slowly, the resulting crystals are very different; they are monoclinic prisms (see Fig. 39, B) whose specific gravity is 1.96–1.98 (water = 1), and which melt at 120° . Hence sulphur is said to be dimorphous. The second variety of crystals may be prepared as follows:

EXPERIMENT 36. Put about 20 gm. of ordinary commercial sulphur in a large crucible, heat it cautiously until the whole mass is completely liquefied, let it cool until a crust forms over the surface, break the crust, and pour the remaining liquid into a beaker filled with cold water. The sides of the crucible will be lined with slender, prismatic crystals, whose forms may be clearly seen by the help of a small lens. The portion which was poured into the cold water will be of a dark brown color and remarkably elastic. It may be kneaded like dough, and even drawn out into fine threads; but by long standing or through persistent kneading it will assume the attributes of ordinary sulphur. If we adhere to the principle laid down on page 12, that a substance is known only by its attributes, it

would appear that these two products, so different in their physical attributes, must be different substances. But according to the researches of Lavoisier, sulphur is an element. Then how can an element change its attributes and yet be recognized as such?

When an element assumes two forms, there are reasons for believing that the difference between them is due to the fact that the molecules are made up of different numbers of atoms. When substances show such modifications they are said to be *allotropic*. Allotropy is another argument for the atomic constitution of matter, for if sulphur, e.g., were a perfectly blended mass and not an aggregation of atoms, it is difficult to understand how it could display these allotropic modifications.

88. Allotropy, and the Constitution of Gaseous Molecules.—We have accepted the formula, $\text{Density} = \frac{\text{Mol. Wt.}}{2}$

The density of sulphur vapor between 800° and $1,000^{\circ}$ is 31.83 ($H = 1$). By substitution we have,

$$31.83 = \frac{\text{Mol. Wt.}}{2} \quad \therefore \text{Mol. Wt.} = 63.66$$

The atomic weight of sulphur is 31.83.

$$\therefore \frac{63.66 \text{ (Mol. Wt.)}}{31.83 \text{ (At. Wt.)}} = 2$$

Hence a molecule of sulphur vapor at from 800° to $1,000^{\circ}$ contains two atoms. Now, the vapor density between 448° and 500° , is 127.32. By substitution we have,

$$127.32 = \frac{\text{Mol. Wt.}}{2} \quad \therefore \text{Mol. Wt.} = 254.64$$

$$\therefore \frac{254.64 \text{ (Mol. Wt.)}}{31.83 \text{ (At. Wt.)}} = 8$$

Hence the molecule of sulphur vapor between 448° and 500° contains 8 atoms. The determination of the molecular weight of a substance from its vapor density is applicable only to gases or substances which can be vaporized without altering the molecule.

89. Allotropy, and the Weight of Molecules of Solids.—The molecular weight of a substance which is solid under ordinary conditions must be obtained by other methods.

It has long been known that the normal boiling or freezing point of a liquid may be altered by dissolving a quantity of some solid in it. Thus pure water freezes at 0° and boils at 100° , but if common salt be dissolved in it, the freezing point of the mixture will be *below*, and the boiling point *above* the normal. It was discovered by Raoult that *a definite relation obtains between the freezing point of a liquid and the quantity and nature of the dissolved substance*. It has been shown experimentally that the *degree* of depression of the freezing point depends upon (a) the quantity and the nature of the solvent, and (b) the quantity and nature of the solid dissolved; in other words, *the amount of depression produced upon a given quantity of any solvent by any given substance, is proportional to the quantity of substance; but a given quantity of substance will produce unequal depression in like quantities of different solvents*. Thus 1 gm. of salt dissolved in 100 gm. of acetic acid produces a depression of the freezing point different from that produced by 1 gm. of salt in 100 gm. of water, or any other solvent. This depression is therefore a specific amount, called the specific depression of the freezing point. *The specific depression is the depression produced by 1 gm. of substance in 100 gm. of solvent*.

It has been discovered that the specific depression for any substance in *any given solvent*, when multiplied by its molecular weight gives a product, C , which is nearly constant

for that solvent. This is made apparent in the following tables.

TABLE V

When the solvent is acetic acid:

FORMULA	SPECIFIC DEPRESSION	MOL. WT.	MOL. WT. $\times$ SPEC. DEP. = C
CS ₂	0.5050	76	76 $\times$ 0.505 = 38.4
CHCl ₃	0.3247	119.5	119.5 $\times$.3247 = 38.8
C ₂ H ₅ OH	0.3851	94.0	94 $\times$ 0.3851 = 36.2
SO ₂	0.6015	64	64 $\times$ 0.6015 = 38.5
			C (average) = 37.9

TABLE VI

When the solvent is water:

FORMULA	SPECIFIC DEPRESSION	MOL. WT.	MOL. WT. $\times$ SPEC. DEP. = C
C ₂ H ₄ O ₂	0.3162	60	60 $\times$ 0.3162 = 18.97
NH ₃	1.1705	17	17 $\times$ 1.1705 = 18.80
CuSO ₄	0.1153	159.7	159.7 $\times$.1153 = 18.41
FeSO ₄	0.1221	152.1	152.1 $\times$.1221 = 18.57
ZnSO ₄	0.1149	161.5	161.5 $\times$.1149 = 18.54
			C (average) = 18.65

It is evident that the constant $C = (\text{Mol. Wt.} \times \text{Spec. Dep.})$ is approximately 38,* when the solvent is acetic acid, and approximately 18.5 when the solvent is water.

The results in Tables V and VI show that the constant C has a specific value for each of these solvents. This value of C for any solvent is ascertained by determining the specific depression of a large number of compounds in that solvent, and averaging the results.

* More extensive tables show it to be approximately 38.8.

The following table shows the accepted value of C for four solvents.

TABLE VII

SOLVENT	MOL. WT. $\times$ SPEC. DEP. = C
Water.....	18.5
Acetic acid.....	38.8
Benzene	49.0
Naphthalene	71.0

A general expression for ascertaining molecular weight is as follows:

Let C = depression constant for a given solvent.

“ M = molecular weight of any solid substance.

“ S = the observed specific depression.

We shall have, $S \times M = C \therefore M = \frac{C}{S}$

To find the molecular weight of a substance, therefore, we have only to divide the constant of the solvent, C , by the specific depression.

Applying this formula to the first two members of Table V we have

$$M = \frac{38.8}{0.5050} = 76.8$$

The known molecular weight of $CS_2 = 76.0$

$$M = \frac{38.8}{0.3247} = 119.4$$

The known molecular weight of $CHCl_3 = 119.5$

In order to apply this method in determining molecular weights, it is necessary to determine the value of C for various solvents, because many substances whose molecular weights are sought do not dissolve in such substances as acetic acid, and water.

The specific depression for sulphur dissolved in naphthalene is 0.265° . Substituting in the formula, $M = \frac{C}{S}$, we shall have

$$M = \frac{71}{0.265} = 267.9:$$

$$\frac{267.9 \text{ (Mol. Wt.)}}{32 \text{ (At. Wt.)}} = 8.3+$$

This indicates that the molecule of solid sulphur contains 8 atoms.

PHOSPHORUS, P (AT. WT. 31)

90. This element was discovered by Brandt, a Hamburg merchant, in 1669. About one hundred years later Gahn and Scheele discovered it in bones, and since that time bones have been the chief source from which the commercial supply is obtained. The process of obtaining phosphorus consists essentially in reducing phosphorus oxide with charcoal

91. Preparation of Phosphorus. — Calcined bones are pulverized and covered with dilute sulphuric acid. The compound containing the phosphorus dissolves in the acid and this liquid is drained off, evaporated to dryness, and the residue heated to redness.

The resulting mass is mixed

with about one-fifth of its weight of charcoal, put into earthen retorts, A, Fig. 40, and again heated to bright redness. The phos-

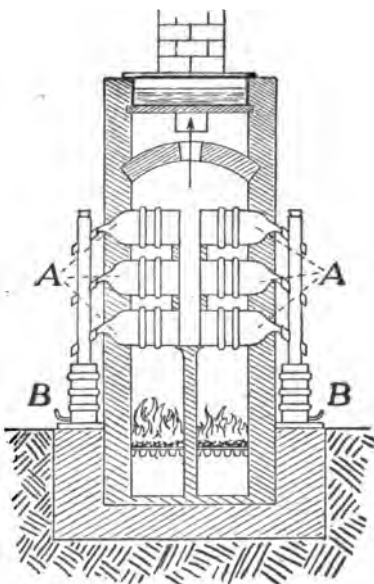


FIGURE 40

phorus oxide is reduced, the phosphorus distills over into the receivers, B, and is collected under water. The fundamental reaction may be expressed by the graph,



92. Properties.—The freshly prepared phosphorus is a colorless or pale yellow, waxy solid which has a peculiarly penetrating odor. Ordinary phosphorus is practically insoluble in water, but dissolves readily in carbon bisulphide. It

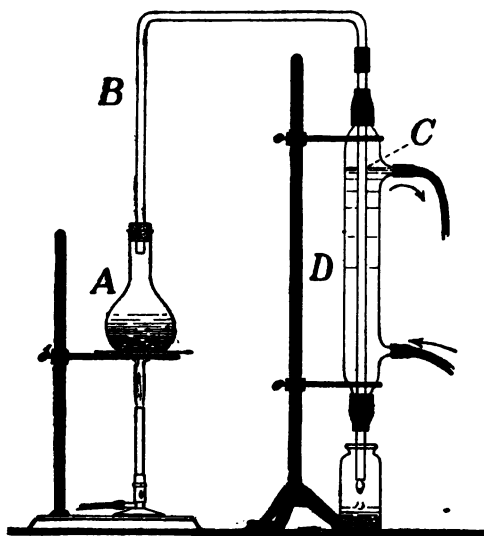


FIGURE 41

is exceedingly poisonous. One grain in a finely divided state is sufficient to kill an adult. Workmen in factories where it is used sooner or later suffer from a peculiar decay of the lower jaw-bone, known as "phosphorus necrosis." It possesses a remarkable affinity for oxygen. When rubbed or exposed to moist air, it becomes more or

less luminous and heat is evolved. When a certain temperature is reached it bursts into flame. This is due to the combination of the phosphorus with the oxygen of the air. The luminosity of phosphorus may be shown in a beautiful manner by utilizing the apparatus shown in Fig. 41.

EXPERIMENT 37. *Caution! Always cut phosphorus under water. Do not handle the phosphorus with the fingers. It*

may ignite and produce deep and very painful burns which are slow to heal. Put a small piece of phosphorus into the flask A, add 100 or 150 cc. of water, acidify it with from 10 to 20 cc. of dilute sulphuric acid (1 : 3), connect the apparatus as shown in the cut, and heat the liquid in A until it boils. If the experiment is conducted in a darkened room, a luminous zone will appear at B, travel along the horizontal arm of the connecting tube, and thence down to the cooler D, where it will reach its greatest intensity at C.

93. Red Phosphorus.—When ordinary phosphorus is heated to 250° or 260° in an atmosphere free from oxygen, it forms a dark red-brown, odorless, tasteless powder (called red or amorphous phosphorus), whose specific gravity at ordinary temperatures is 2.10 (water = 1). It does not change in the air, and does not become luminous when rubbed or heated gently. It melts and ignites at 260° . In short, it does not possess any of the attributes of ordinary phosphorus. These facts suggest that we have here an allotropic modification. This suggestion is confirmed by the fact that red phosphorus may be transformed into the ordinary variety by heating it above 260° out of contact with air. The density of ordinary phosphorus between 500° and $1,000^{\circ}$ is .62, and since

$$D = \frac{\text{Mol. Wt.}}{2}; \text{Mol. Wt.} = 124; \text{and } \frac{124 (\text{Mol. Wt.})}{31 (\text{At. Wt.})} = 4, \text{ the}$$

number of atoms in the molecule. Therefore the formula of the molecule of phosphorus at a temperature of from 500° to $1,000^{\circ}$, is P_4 . At white heat the density is 31. Its molecule is then P_2 . The specific depression of the freezing point for yellow phosphorus in benzene is 0.392° .

By substituting in the formula, $M = \frac{C}{S}$, we have,

$$M = \frac{49^*}{0.392} = 125 \quad \therefore \frac{125 (\text{Mol. Wt.})}{31 (\text{At. Wt.})} = 4 +$$

*See Table VII.

THE EFFECTS OF OXIDATION UPON SULPHUR AND PHOSPHORUS

94. The Combustion of Phosphorus in Oxygen.—

EXPERIMENT 38. Clean a piece of yellow phosphorus by scraping it under water, cut off a piece about the size of a pea, dry it quickly between filter papers, put it immediately into a clean, dry deflagrating spoon whose shaft has been passed through the center of a piece of cardboard of sufficient size to cover the cylinder, ignite the phosphorus, plunge it into the cylinder of oxygen, B, (Fig. 8, p. 31) and adjust the cardboard so that the fumes do not escape. The phosphorus will burn with intense brilliancy and the evolution of dense white fumes. These fumes are an oxide of phosphorus, since only oxygen and phosphorus were present. The reaction is expressed by the graph, $2P + 5O = P_2O_5$.

If the cylinder is perfectly dry, the oxide will settle upon the bottom and sides in flaky white masses. Now remove the spoon, add about 50 cc. of distilled water, quickly close the cylinder with a glass plate, and let it stand until the white fumes are completely absorbed. Mark it Solution I.

95. The Combustion of Sulphur in Oxygen.—

EXPERIMENT 39. Put a small lump of sulphur in a clean deflagrating spoon equipped as described in Experiment 38, hold it in the flame of a burner until the sulphur ignites, and plunge it into receiver B, as directed for phosphorus. It will be observed to burn with a blue flame. Add about 50 cc. of water to the cylinder, quickly cover it with a glass plate, and let stand for several hours; or shake the contents vigorously, taking care that the cylinder be kept tight. Mark it Solution II. We found, on page 79, that two atoms of hydrogen combine with one atom of sulphur to form H_2S . This indicates that the sulphur atom acts with a valence of two when com-

binning with hydrogen. If it acts with the same valence when combining with oxygen, the formula of the oxide should be SO . But its vapor density is 32, which gives 64 for its molecular weight. Subtracting 32, the atomic weight of sulphur (one atom could not combine with less weight), we have 32 to be made up by the oxygen, which is just twice the atomic weight of that element. This gives us authority for the graph, $\text{S} + \text{O}_2 = \text{SO}_2$. Here we have another example of variation in valence, and still another is found in the oxidizing of sulphur dioxide, SO_2 , to sulphur trioxide, SO_3 .

96. The Combustion of Sulphur Dioxide in Oxygen.

—When a dry mixture of sulphur dioxide and oxygen is drawn through a tube which contains a small quantity of finely divided platinum heated to redness, active chemical action takes place about the platinum, and the tube is quickly filled with dense white fumes. These fumes must be an oxide of sulphur higher than SO_2 , for the tube contained only SO_2 , platinum, and free oxygen, and the platinum does not enter into combination, and neither sulphur nor oxygen is set free. The chemical action may be expressed by the graph, $\text{SO}_2 + \text{O} = \text{SO}_3^*$. That the gas formed is SO_3 is shown as follows: Its density is 40, which gives a molecular weight of 80. We could have $\text{SO}_3 = 80$, or $\text{S}_2\text{O} = 80$. The second interpretation is impossible, since S_2O would be a reduced form of SO_2 , and oxygen was not set free in the experiment.

97. Carbon Dioxide in Water.—Introduce about 50 cc. of distilled water into a third cylinder, C, and allow a stream of carbon dioxide to bubble through the liquid for ten minutes and mark it Solution IV.

*Crystals of SO_3 may be obtained by boiling a few cubic centimeters of fuming sulphuric (Nordhausen) acid, and collecting the distillate, which crystallizes, in a perfectly dry receiver. The distillation should be carried on by the instructor. Some of the crystals should be dissolved in water, marked Solution III, and kept for further study.

98. Properties of the Oxides of Sulphur, Phosphorus, and Carbon.—We now have four colorless liquids which contain respectively P_2O_5 , SO_2 , SO_3 , and CO_2 in solution. Taste a small quantity of each solution. Each will be found to have a more or less sharp, sour flavor. Drop a small piece of blue litmus paper into each; it will be changed immediately to a pale red. Solutions of the four oxides, prepared in a similar way, possess at least two attributes in common: their sour flavor, and their effect upon litmus paper. Test very dilute (1 : 20) hydrochloric, nitric, and sulphuric acids in the same way. They, too, will show the sour flavor and turn the blue litmus paper red. Let us accept for the present these two attributes as characteristic of *acids*. Then we may say that these oxides of phosphorus, sulphur, and carbon, when dissolved in water, give rise to solutions which possess acid properties.

It will be of interest to study the action of oxidation upon the common metals with which we have dealt: iron, zinc, magnesium, copper, sodium, etc. Before taking up this study, it will be advantageous to examine two or three of these elements more in detail.

SODIUM, NA (AT. WT. 23.05)

99. This element, isolated by Davy, in 1807, does not occur free in nature, but is found in a variety of compounds, chief among which is common salt. This substance is found in immense quantities and widely distributed. It is a constituent of sea-water, salt lakes, and many springs. In the form of rock salt, it occurs at varying depths in the earth and over wide areas. Salt deposits occur in England, Poland, Austria, Germany, New York, Kansas, Michigan, Virginia, Louisiana, and elsewhere. A great many other compounds of sodium are prepared from salt.

100. Preparation of Sodium.—The free element, sodium, may be prepared by electrolyzing fused sodium hydroxide, or in the following manner:

An intimate mixture of sodium carbonate, coal, and limestone is placed in iron cylinders and distilled at a high temperature. The fundamental reaction may be expressed by the graph,



The vapor of sodium distills over and is condensed to a liquid which is collected under petroleum. The crude product is then remelted under petroleum, and cast into bars.

101. Properties of Sodium.—The pure substance is a silver-white metal of brilliant luster, and, at ordinary temperature, about as hard as beeswax. It is lighter than water, its specific gravity being 0.972 (water = 1). It melts at 95.5° and, in the absence of air, volatilizes at 742° , forming a colorless vapor. It possesses an extraordinary affinity for oxygen, so that it must be kept under a liquid, such as naphtha, which does not contain oxygen even in combination. The great affinity of sodium for oxygen may be shown by the following experiment.

EXPERIMENT 40. *Caution! Hold sodium with pincers. Keep it dry. Use a very small piece.* Introduce about 50 cc. of tepid water into a 200 cc. cylinder. Cleanse a piece of sodium not larger than a pea (by pressing it between dry filter papers), drop it into the cylinder, keeping the head away from it, and quickly close the cylinder with a glass plate. Vigorous chemical action takes place, and a gas is given off. If the water is very hot, the gas will ignite. The identity of this gas may be established in the following experiment.

EXPERIMENT 41. *Caution! See above.* Clean a piece of sodium, not larger than a pea, by folding filter paper about it.

Put it into the deflagrating spoon C, Fig. 42, wrap the bowl in copper gauze, so that the sodium cannot escape, fill the cylinder A with water, invert it over water in D, hold the cylinder with the left

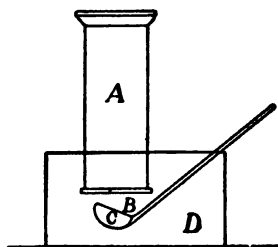


FIGURE 42

hand, and with the right quickly plunge the bowl of the spoon under its mouth. Vigorous chemical action takes place and a gas is given off. The escaping gas will collect in the upper part of the cylinder, and it may be examined, in the usual manner, as to odor, color, combustibility, and power to support combustion. Is it hydrogen? Test the water with red litmus paper.

POTASSIUM, K (AT. WT. 39.15)

102. This element was first isolated by Davy, in 1807. Like sodium, it does not occur free in nature, but is found in combination with other elements. It is present in complex combinations in the feldspar and mica of most granites. As these rocks are decomposed, simpler compounds of potassium are formed, which are soluble. One of the most valuable of these potassium compounds for plant food is saltpeter, a compound of potassium and nitric acid. It occurs in natural deposits in Egypt, Germany, Chili, the East Indies, and many of the South Pacific Islands.

103. Properties of Potassium.—Potassium is very similar to sodium in both its physical and chemical attributes. At ordinary temperatures it is a silver-white metal whose specific gravity is 0.865. It melts at 62.5 and is vaporized at 667°, in the absence of air, forming a pale green vapor. Like sodium, it shows a strong affinity for oxygen, and, like sodium, must be kept under naphtha or petroleum. Experiment 41 may be performed with this potassium with the same precautions, and

with identical results. Sodium and potassium are so much alike that usually one may be substituted for the other in chemical processes.

MAGNESIUM, Mg (At. Wt. 24.36)

104. Preparation and Properties.—This element was first isolated by Bussy, later by Bunsen. It does not occur free in nature, but is widely and abundantly distributed in compounds, among which are dolomite, olivine, talc, asbestos, meerschaum, and carnallite. Its compounds are also found in sea-water, and in the water of many mineral springs. It is usually prepared by passing an electric current through fused magnesium chloride, when the magnesium separates and collects at the negative pole.

An outline of the apparatus used in this method of preparing the magnesium is shown in Fig. 43. The cylinder A (which is shown in cross section) is made of iron. B is a porcelain cylinder open at the base; D, D, and E are openings into the cylinders A and B, which allow a free ingress and egress of gases and thus equalize the gaseous pressure in the upper portions of these cylinders. C is a heavy carbon rod which dips into the liquid in A.

Process. Magnesium chloride, or a compound (carnallite) which contains it, is put into the cylinder A and melted by external heat. A strong electric current is then passed from C to A, through the fusing chloride.

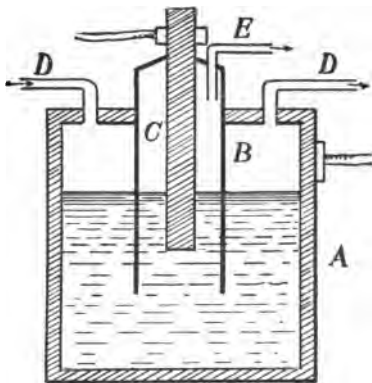


FIGURE 43

The chloride is separated into magnesium, and chlorine, and the former collects upon the surface of the liquid in A, and is kept from oxidizing by some inert gas which is introduced into the outer cylinder through D. The chlorine of the decomposed chloride is liberated on the surface of the carbon rod C, and escapes from the cylinder B through the exit tube E. The magnesium is then removed and purified by dis-

tilling it in an atmosphere of hydrogen. In a pure state it is a silver-white metal of high luster, which tarnishes very rapidly in moist air. It melts at a dull red heat and distills at any temperature above this. It is so easily combustible that it may be ignited with a match. The intensely brilliant, blinding light which results is found to be especially rich in the chemical (actinic) rays so useful in photography. "Flash light" powder is made of finely powdered magnesium.

CALCIUM, CA (AT. WT. 40.1)

105. Preparation and Properties.—Calcium was isolated by Davy, in 1808, by electrolyzing fusing calcium chloride. It was afterwards prepared in much larger quantities and in a purer form by Bunsen and Matthiesen. This element is the fifth most abundant in nature, though it does not occur free. It is a constituent of a great variety of minerals, some of the most common of which are calcite (the principal mineral of limestone, marble, chalk, etc.), dolomite and gypsum. It is a yellow, lustrous, soft and ductile metal, which has a specific gravity of 1.55 to 1.60. It is permanent in dry air, but tarnishes readily when moist, combining with water at ordinary temperatures with the liberation of hydrogen. It melts at a dull red heat, and burns in oxygen with an intense reddish flame.

OXIDATION OF METALLIC ELEMENTS

We may now study the oxidation of these and some other metallic elements, remembering that chemical activity which depends upon the air is usually due to the oxygen.

106. Oxidation of Metallic Sodium.—*Caution! Do not touch sodium with the fingers. Use pincers. See that all parts of the apparatus are perfectly dry.*

EXPERIMENT 42. Dry a piece of sodium between filter papers, cut off the outside coating to remove the oil, put the clean portion, which should not be larger than a pea, into a clean

porcelain dish of approximately 8 cm. diameter, supported on a wire gauze. Heat the dish until the sodium fuses to a globule, and maintain the fusion until all the sodium is transformed into a uniformly white mass. The oxidation may be facilitated by stirring the molten mass frequently, so that fresh portions of metal shall come into contact with the air. (If all of the oil was not removed from the sodium, the product in the dish will be more or less blackened by the separation of carbon from the oil.) Allow the dish to cool, digest the residue with 15 or 20 cc. of distilled water whose temperature has been taken previously, note any increase in the temperature, filter off any carbon or other insoluble impurity, and keep the clear filtrate for further examination. Mark it Solution A.

Sodium acts with unit valence under ordinary conditions, and since oxygen is bivalent we write the following graph as an expression of the oxidation



107. Oxidation of Metallic Potassium.—*Caution! Use the same precaution in handling potassium as in handling sodium.*

EXPERIMENT 43. Dry a small piece of potassium between filter papers, cut off the outside coating to remove the oil, put a piece about the size of a pea into a clean porcelain dish, and proceed as directed in Experiment 42. Mark the clear filtrate B, and keep it for further study. Potassium, like sodium, acts with unit valence, so the chemical change is expressed by the graph, $2\text{K} + \text{O} = \text{K}_2\text{O}$.

108. Oxidation of Magnesium.—**EXPERIMENT 44.** Put about 0.1 gm. of clean magnesium ribbon or magnesium powder in a porcelain crucible, cover, and heat until the contents ignite. A pure white amorphous powder is produced, which is magnesium oxide. It was shown, on page 89, that magnesium

acts with a valence of two; hence we may write the graph, $\text{Mg} + \text{O} = \text{MgO}$. Mark the powder C, and keep it for further study.

109. Oxidation of Calcium.—**EXPERIMENT 45.** Put a small piece of metallic calcium into a porcelain crucible, and proceed with its oxidation as directed for magnesium. Calcium is bivalent in its combining activity, so we shall have, $\text{Ca} + \text{O} = \text{CaO}$. Calcium oxide is a pure white, infusible, amorphous powder. Put this powder into a small beaker, add about 50 cc. of water whose temperature has been taken previously, stir well, and note any increase in the temperature of the mixture. Warm the contents for about five minutes, filter off any insoluble portion and set the clear filtrate aside in a closed vessel marked D. Keep the solid residue for further examination.

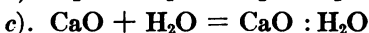
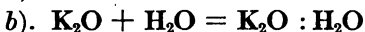
110. Preparation of Calcium Oxide from Calcium Carbonate.—If metallic calcium is not at hand, its oxide may be prepared by heating precipitated calcium carbonate in a blast-lamp flame until it ceases to lose weight. CaCO_3 (heated) = $\text{CaO} + \text{CO}_2$ (see Appendix). Pure calcium oxide may also be had from dealers in laboratory supplies.

As the result of the oxidation of sodium, potassium, magnesium, and calcium we have the four oxides, Na_2O , K_2O , MgO , and CaO .

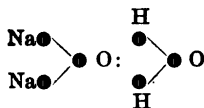
111. The Solution of the Metallic Oxides in Water.—Now test the solutions A, B, and D with both blue and red litmus paper. These solutions change the red litmus to blue, which is the direct opposite of the influence exerted by the oxides of phosphorus, sulphur, and carbon. (See p. 134.) The oxide of magnesium is not very soluble in water, but if a piece of red litmus be moistened and a small quantity of this oxide placed in contact with it, the paper will slowly change to

blue. Taste each solution; its flavor is not sour. These compounds are called *alkalis*, and their action on red litmus is termed the "alkaline reaction."

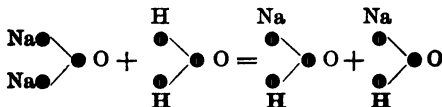
Is the alkaline reaction due to the oxides of the metals, or to some compound which results from their interaction with water? We already have some evidence that compounds were formed in preparing solutions A, B, and D, for on mixing the respective oxides with water, we observed an appreciable rise in temperature, which indicates a chemical action. It must have been a synthetic, additive process, since neither hydrogen nor oxygen was set free. The qualitative course of the reactions may be expressed by the hypothetical graphs,



A wider interpretation of these new compounds is necessary. In *a*), the two constituent oxides, Na_2O and H_2O , have the valences of the elements satisfied, and possess in consequence no combining power. This is seen clearly in the graph,



Since combination occurred without any loss of hydrogen or oxygen, it follows that there must have been a readjustment of the atoms, and the nature of this rearrangement was conditioned by the valences of the participating elements. It has been established already that H and Na are univalent, while oxygen is bivalent. The following graph expresses the only combination in harmony with these valences:



Any other combination will give either free hydrogen or free oxygen.

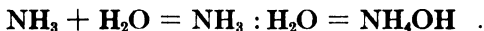
The probable course of the reactions is as follows:

- a). $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}$, Sodium hydroxide.
- b). $\text{K}_2\text{O} + \text{H}_2\text{O} = 2\text{KOH}$, Potassium hydroxide.
- c). $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$, Calcium hydroxide.

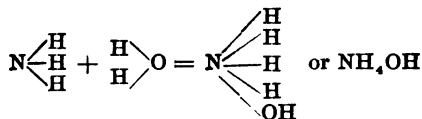
When a metal is combined with the group "OH," it is said to form a *hydroxide*; and the group "OH" is spoken of as the "hydroxyl" group, or radical. Therefore we may say that the hydroxides of sodium, potassium, calcium, and magnesium are alkaline hydroxides.

There are three hydroxides not included in the above list which also possess strong alkaline properties.

Generate some ammonia as directed on page 68, using the apparatus shown in Experiment 22, and collect it in about 50 cc. of water. Test the reaction of the liquid with litmus paper. Does it possess the alkaline reaction? Adopting the preceding hypothesis, we have,



It was pointed out, under the discussion of valence (p. 99), that nitrogen possesses a variable valence. The above reaction may be explained in terms of this variation, if we suppose that this element can act with a valence of five.



We shall discover later that there is every deductive reason to believe that ammonium hydroxide is formed. It has never

been isolated, because it is so exceedingly unstable that it breaks up spontaneously into water and ammonia.

Before discussing the remaining hydroxides, it will be necessary to study two new elements.

BARIUM, BA (AT. WT. 137.4)

112. Properties of Barium.—This element is not found free in nature, but occurs in two chief minerals—heavy spar and witherite. The pure element is a yellow metal which melts at a red heat but does not vaporize. It is permanent in dry air, but oxidizes readily in moist air.

STRONTIUM, SR (AT. WT. 87.6)

113. Preparation and Properties of Strontium.—This element does not occur free in nature, but is found chiefly in strontianite, a mineral which is found in abundance near Strontian in Scotland; hence its name. (It occurs also in small quantities in sea and mineral waters, in gypsum, and some other minerals of less general distribution.) The free element is a yellow, ductile metal which melts at a dull red heat.

114. Preparation of Barium and Strontium Hydroxides.—Digest the respective oxides in approximately 50 cc. of distilled water whose temperature is known, mark any elevation in temperature, and test the respective filtrates with red litmus paper. They will show a strong alkaline reaction. The solution of these oxides in water may be expressed by the graphs,



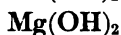
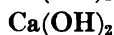
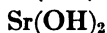
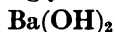
115. The Alkaline Hydroxides.—We now have before us seven hydroxides, all of which possess strong alkaline prop-

erties. They may be classified, according to their solubility in water, into two groups:

Readily soluble.

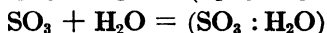
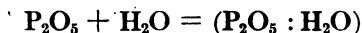


Sparingly soluble.

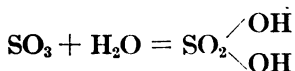
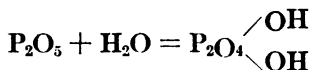


The members of the first group are commonly called the *alkali* hydroxides; the second, the *alkali-earth* hydroxides.

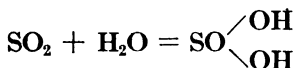
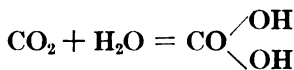
116. The Acid Hydroxides.—We have discovered in the preceding pages that the oxides of phosphorus, sulphur, and carbon dissolve in water with greater or less ease, and that the solutions show the *acid* reaction toward litmus. Prepare (if necessary) fresh portions of the solutions of P_2O_5 , SO_2 , SO_3 , and CO_2 , as previously directed, put them into four flasks marked respectively A, B, C, and D, and boil until only 2 or 3 cc. of fluid remain in each. Test this fluid with blue litmus. It will be found that the solutions of P_2O_5 and SO_3 still show a strong acid reaction, while those of SO_2 and CO_2 do not. This shows that the solution of SO_2 or CO_2 in water is not a stable one, while the other two oxides resist the decomposing power of boiling water. This deportment naturally suggests the question, do these oxides combine with the water when they are dissolved by it? It is noteworthy that P_2O_5 and SO_3 dissolve with the evolution of much heat. This shows chemical action. Since neither hydrogen nor oxygen was set free, this combination must have been directly additive. The qualitative course of the reaction may be expressed by the graphs,



This hypothesis finds confirmation in the observations already made, that both phosphorus and sulphur change their valence with ease. As we have no experimental data upon which to base the proportions assumed in the equations above, let us accept them for the present, and prove or disprove them in the succeeding chapter. By expressing these formulas in forms analogous to those used for the alkaline hydroxides, we have,



If carbon dioxide united with the water, the resulting compound must have been unstable. If such a combination occurred, we have some data upon which to determine the proportion in which the elements combined. It has been pointed out that one molecule of carbon dioxide is combined with one molecule of calcium oxide in calcium carbonate, i.e., $\text{CaO} + \text{CO}_2 = \text{CaO} : \text{CO}_2$. If we substitute one molecule of hydrogen oxide for the calcium oxide, we shall have $\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{O} : \text{CO}_2$. This is of course purely hypothetical. The exact compound is so unstable that it has never been isolated. The same is true of the solution of sulphur dioxide in water. These hypothetical compounds may be written,



Phosphorus, sulphur, and carbon belong to a group of elements commonly called the non-metals. Barium, strontium,

calcium, magnesium, sodium, and potassium are metals in the common acceptation of the term. Hence,

1. The hydroxides of these non-metals are acids, and
2. The hydroxides of the alkali and alkali-earth metals are alkalis.

117. The Oxides of Nitrogen.—The oxides of nitrogen show a deportment somewhat similar to that of the oxides of the non-metals, and should therefore be studied in this connection. It has already been pointed out that nitrogen does not combine directly with oxygen under ordinary conditions. Indirect methods must be used, whose action will be made clear subsequently.

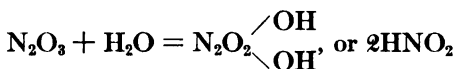
I. *Nitrous oxide*.—EXPERIMENT 46. Use the apparatus for the preparation of oxygen (p. 28), substituting a 100 cc. flask. Put about 20 gm. of ammonium nitrate into the clean, dry retort, connect as shown in the cut (Fig. 4), heat the flask gently until a vigorous flow of gas is obtained, and then collect two or three cylinders of it. Note its odor, color, solubility in water, and power to support combustion. It supports combustion with almost as much vigor as pure oxygen. This is due to the very feeble union of the oxygen with the nitrogen, so that the oxygen becomes available easily for other action.

Its vapor density is 22; hence its formula must be N_2O , for no other combination of oxygen and nitrogen will have a molecular weight of 44 (twice the vapor density, see p. 77). This gas possesses very pronounced physiological properties. When inhaled in small quantities, it produces a characteristic exhilaration which has given it the name "laughing gas." If a sufficient amount of the gas be taken, the period of exhilaration or intoxication is succeeded by one of unconsciousness and general anaesthesia.

II. *Nitric oxide, or nitrogen dioxide*.—This is another colorless oxide of nitrogen, which is usually given off when nitric acid acts upon metals.

EXPERIMENT 47. Into a 200 cc. flask fitted with a funnel tube and a delivery tube, put about 10 gm. of copper cuttings. Add about 15 cc. of strong nitric acid and collect the escaping gas over water. Observe its solubility in water, odor, etc. It will be found to support the combustion of phosphorus, but a pine splint will not burn in it. Its most remarkable attribute is its power to absorb oxygen, with the formation of red-brown fumes, NO_2 . The vapor density of nitric oxide is 14.98. Its formula must be NO , for there is no other combination of oxygen and nitrogen which could give the molecular weight, 29.96.

III. Preparation of nitrogen trioxide, N_2O_3 .—This compound is difficult to prepare, because it is unstable, decomposing at ordinary temperatures into NO and NO_2 . It is usually prepared by adding a saturated solution of cane sugar, drop by drop, to concentrated nitric acid (specific gravity 1.35), and condensing the escaping gas in a flask which is surrounded by a mixture of ice and salt. Nitrogen trioxide is a green liquid. Its solution in water gives the acid reaction. In this respect it is like an oxide of a non-metal. The course of the reaction may be expressed by the hypothetical graph,



IV. Preparation of nitric acid.—Perform this experiment under the hood.

EXPERIMENT 48. Use the apparatus shown in Fig. 44. A is a 200 cc. glass retort whose neck extends deep into the large test tube B. This tube, which serves to cool the distillate, should be partly immersed in a large beaker of cold water. Put about 20 gm. of potassium nitrate (saltpeter) into the retort, add an equal weight of strong sulphuric acid, and heat the mixture gently until 5 or 6 cc. of distillate have been col-

lected. The pure acid is a colorless liquid, but it is usually yellow from the presence of oxides of nitrogen, e.g., NO_2 . It has a suffocating odor, and is exceedingly corrosive to all animal tissue. It imparts a deep yellow color to the skin, nails, silk, feathers, etc.

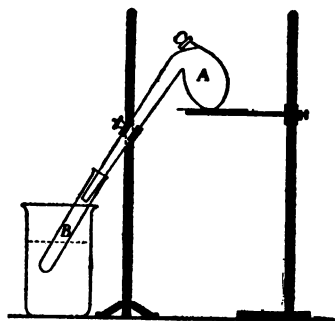


FIGURE 44.

That this acid contains an oxide of nitrogen may be readily shown by dropping a lump of glass-wool or a stick dipped in strong nitric acid into a vessel filled with sulphur dioxide. Red fumes will at once fill the jar. These may be identified by the

odor and color. Coincident with these changes white crystals will be deposited upon the sides of the cylinder. On adding water the crystals dissolve with much energy, and sulphuric acid may be found in the liquid.

Summary.—The facts which have been brought out in the preceding chapters point to the following conclusions:

1. Valence may vary, since it is not an absolute property of atoms.
2. Equivalent quantities of two elements may be expressed by the equation,

$$\frac{MW}{V} = \frac{M'W'}{V'}$$

in which M , V , and W are the atomic weight, valence, and gross weight respectively of one element (A); and M' , V' , and W' are the atomic weight, valence, and gross weight respectively of any other element (B).

3. Oxidation and reduction are reciprocal terms. In its broadest use, the one means increase and the other decrease in valence.

4. The oxides of certain non-metals when dissolved in water produce acids. The oxides of the alkali and the alkali-earth metals when dissolved in water produce alkalis.

EXERCISES

1. 1.71 gm. of bromine dissolved in 100 cc. of acetic acid give a specific depression of 0.251° ; determine the weight of the molecule.

2. Does this result confirm the theory that elements exist in molecules?

3. 2.19 gm. of iodine in 100 gm. of naphthalene give 0.272° for the specific depression; what is the weight of its molecules?

4. What should be the specific depression of hydrogen chloride dissolved in acetic acid?

5. Calculate the specific depression for common salt (NaCl) dissolved in water.

6. How could it be shown that barium carbonate has the formula BaCO_3 ?

7. What makes vinegar sour?

8. What evidence have we that the air is a mechanical mixture?

CHAPTER IX

THE STRUCTURE OF METALLIC AND NON-METALLIC OXIDES

The purpose of this chapter is to discover the fundamental differences in the structure and chemical relations of acids and alkalis. Both have been classified as hydroxides, because they were formed by the same essential processes, namely:

1. The oxidation of some specific element, and
2. The combination of this oxide with water.

Is there a fundamental difference in the structure of the two types of substances? Two methods, electrolysis and neutralization, may be employed to obtain this information.

118. The Deportment of Acids toward the Electric Current.—EXPERIMENT 49. Employ the apparatus shown in Experiment 20. We must first ascertain the deportment of pure water toward the electric current. Fill the tubes X and Y with pure distilled water, connect the apparatus as directed in Experiment 20, and allow the current to flow for approximately 20 minutes. If the water is pure there will be practically no gas in either tube. Now fill the tubes with a solution of dilute sulphuric acid (1 : 20), proceed as before, and read and record the gas volumes. Test the properties of these gases. (See Experiment 20.)

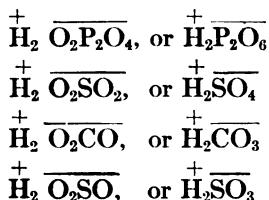
Repeat the process, using successively solutions of hydrochloric, hydrobromic, nitric, and phosphoric acids. Care must be taken that the current always flows in the *same* direction, i.e., from X toward Y, otherwise there will be no basis for

comparisons. These experiments should yield the following results:

TABLE VIII

ACID	TUBE Y	TUBE X
Sulphuric	Hydrogen	Oxygen.
Hydrochloric	Hydrogen	Chlorine.
Hydrobromic	Hydrogen	Bromine.
Nitric	Hydrogen	An oxide of nitrogen.
Phosphoric	Hydrogen	Oxygen.

The presence of hydrogen in tube Y in each case shows that it is a constituent of all these acids. It migrates with the current; and may therefore be designated positive hydrogen, $\overset{+}{\text{H}}$. The content of tube X varies with the acid used; each gives its own characteristic product. These products, called radicals, possess negative electrical properties. Let them be represented by the symbol R, then the general structure of an acid may be represented by the formula, $\overset{+}{\text{H}} \bar{\text{R}}$. This is true whether the acid is the hydroxide of sulphur, phosphorus, or carbon, or is composed of hydrogen with chlorine, bromine, etc., with no oxygen. We may conclude from these phenomena that at least one, and perhaps all, of the hydrogen atoms in acids are electrically positive. The hypothetical formulas given on page 145 may be expressed in this wise:

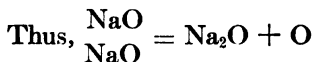


The student should bear in mind that the negative radicals represented by R may decompose in tube X into *other products*; or they may react upon the water in this tube, producing other compounds, for the

migration of the positive hydrogen to tube Y leaves the radical R with at least a part of its valence *unsatisfied*. A readjustment of the atoms would necessarily follow, unless of course the radical is an element. Such a condition is met with in hydrochloric acid. In this case the chlorine is set free and dissolves to a great extent in the water, on which it acts but slowly.

119. The Deportment of the Alkalis toward the Electric Current.—Put dilute solutions of the respective hydroxides tabulated on page 144 into the electrolyzing apparatus and allow the current to pass from X to Y until an appreciable volume of gas is obtained. Tests prove these gases to be hydrogen and oxygen in the proportion of two volumes of hydrogen in tube Y to one volume of oxygen in tube X. It is important to note that the hydrogen apparently traveled *with* the current, while the oxygen opposed it. What do these facts signify? Let two hypotheses be considered:

First, that the NaOH, e.g., splits up into H and NaO. The H migrated with the current to the tube Y, and the NaO to the tube X. Now NaO cannot persist, for Na is univalent, while O is bivalent. Two molecules of it could break up into Na₂O and O.



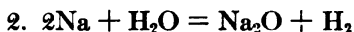
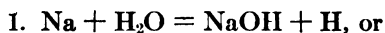
It would require two molecules of NaOH to supply the necessary atoms. This would give two atoms of hydrogen to the tube Y. We would then have,

$$\text{Vol. H : Vol. O} :: 2 : 1$$

This agrees with the experimental results. It is important to note that this hypothesis places the sodium, as sodium hydroxide, in the water in tube X.

Second, let us suppose that the NaOH splits up into Na and OH, and that Na migrates with the current and the OH opposite it. We would then have one atom of Na in tube Y for each molecule of OH carried to tube X. But Na reacts on

water, liberating hydrogen. This may be expressed by two possible reactions;



In either case we would have one atom of hydrogen set free for each atom of sodium which entered into combination. Consequently each atom of sodium which migrated to tube Y would set free one atom of hydrogen from the water on which it reacts. Now the molecule of OH which migrated to the tube X cannot persist, for the same reason that NaO cannot. Either one of two reactions might occur: (1) It might break up into O and H, in which case the volume in X would be twice that in Y, and the gases would consist of equal parts of oxygen and hydrogen; or, (2) two molecules might break up into H_2O , and O. For this reaction two molecules of OH are required. This would require two molecules of NaOH, and would give one atom of oxygen to tube X, and two atoms of hydrogen to tube Y. That is,



It is important to note that this hypothesis will place the sodium as sodium hydroxide in the water in tube Y. Both of these hypotheses will account for the quality and quantity of the gas in each tube. If the first is true, the *hydrogen* in the alkali hydroxides is combined like the hydrogen of acids; if the second is true, the *sodium* in the alkali hydroxide corresponds to the hydrogen of the acids. The first hypothesis gives H^+NaO^- ; the second Na^+OH^- .

In the electrolysis of sodium chloride the sodium migrates *with* the current and is found in the tube Y. This is in harmony with the second hypothesis and gives for sodium hydroxide the structure, Na^+OH^- .

The electrolysis of calcium hydroxide, $\text{Ca}(\text{OH})_2$, gives the same proportion of hydrogen and oxygen as the sodium hydroxide;

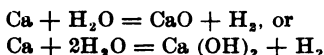
$$\text{Vol. H} : \text{Vol. O} :: 2 : 1$$

Here again two hypotheses are possible.

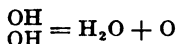
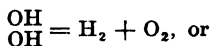
First, the H_2 in the hydroxyl migrated to the tube Y, and the CaO_2 to X. CaO_2 cannot persist, for the same reason that NaO cannot; it could decompose, however, into $\text{CaO} + \text{O}$. This would give us two volumes of hydrogen in Y to one volume of oxygen in X and would place the calcium in tube X.

$$\text{Vol. H} : \text{Vol. O} :: 2 : 1$$

Second, suppose the Ca migrated to the tube Y, and the $(\text{OH})_2$ to tube X. It was pointed out on page 138 that calcium, like sodium, reacts upon water with the liberation of hydrogen. We might have,

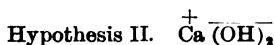
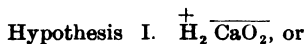


In either case we would have two atoms of hydrogen set free for each atom of calcium used. It is important to note that this would place the calcium as calcium hydroxide in the water in tube Y. The two hydroxyls which migrated to tube X could break up in one of two ways:



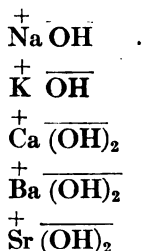
The first is not tenable, for the same reason given for sodium, i.e., the volume of gas in X would double that in Y, and the gases would consist of equal parts of oxygen and hydrogen.

Either hypothesis agrees with the volume and kind of the respective gases. We could have,



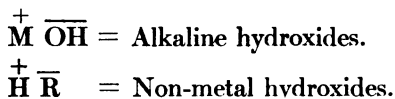
Obviously then the true interpretation depends upon the disposition of the calcium. It will be shown subsequently that the calcium migrates *with* the current to tube Y. This gives $\overset{+}{\text{Ca}} \overline{(\text{OH})_2}$.

Similar experimental data and similar reasoning lead to the conclusions expressed by the following tabulation:



120. General Structure of Acid and Alkaline Hydroxides.—If M stand for any metal in the above table, then $\text{M} \overline{\text{OH}}$ is a general expression for its hydroxide. $\text{H} \overline{\text{R}}$ is the general type of acids.

Placing these two in juxtaposition we have,



This affords us some insight into the fundamental differences in the structure of acid and alkali molecules. It should be kept in mind that $\text{H} \overline{\text{R}}$ also holds for hydrochloric, hydrobromic, and nitric acids, although the first two are not hydroxides.

THE REACTION BETWEEN METALLIC OXIDES AND ACIDS

We are now prepared to examine into the fundamental differences between alkaline and acid hydroxides.

121. Preparation of Materials.—EXPERIMENT 50. Put approximately 5 gm. of copper oxide into a 200 cc. evaporating dish, add about 50 cc. of dilute sulphuric acid (1 : 10), heat the mixture until the copper oxide is completely dissolved (add more acid if necessary), filter off any insoluble residue, and evaporate the clear filtrate to about 50 cc. Cover the dish to

keep out any dust, and set it aside for 12 hours. If crystals do not separate, evaporate the liquid to half its volume, and again set it aside until crystals separate. Drain off the liquid and press the crystals between pieces of blotting or filter paper to dry them. Are they homogeneous? Do they possess the attributes of copper oxide? Of copper? Of sulphuric acid? If they contain copper, it must be in combination, for the crystals have not the attributes of the metal. Dissolve a crystal in 5 or 6 cc. of water, add a few drops of sulphuric acid, and insert a clean knife blade into the solution. It will be coated with copper. Evidently there is copper in combination, but in what combination? The following experiment will help to make the point clear.

122. The Electrolysis of a Copper Compound.—

EXPERIMENT 51. Dissolve about 3 gm. of the well-dried crystals obtained in Experiment 50 in about 150 cc. of distilled

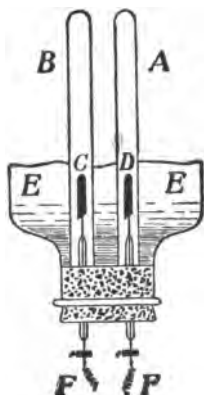


FIGURE 45

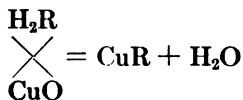
water, and subject the solution to electrolysis. The apparatus shown in Fig. 45 is well adapted to this purpose. Fill the tubes A and B with the copper solution, and pour the remainder into E. If it is not sufficient to cover the electrodes C, D, add more water. Invert the tubes A and B over D and C, as in figure, connect, and pass the current from D to C until at least 5 cc. of gas has accumulated in A. Test the attributes of the gas in A, and note the character of the deposit upon C. The gas in A should possess the attributes of oxygen; the deposit upon C, the attributes of metallic copper. If the current is not too powerful, no appreciable quantity of gas will be collected in B.

This will give us some insight into the new copper com-

pound. It was discovered on page 151 that the sulphuric acid molecule HR gives, upon electrolysis, positive hydrogen and negative oxygen, the hydrogen of the acid migrating with the current, while the negative radical goes in the opposite direction. It was pointed out on page 151 that the negative radical may act upon the water in tube A. In this case oxygen is the product of this secondary reaction. It therefore becomes the representative of R , while the copper becomes the representative of H . Hence in the combining of copper oxide and sulphuric acid, the positive hydrogen of the acid was not incorporated, but the copper has taken the place of this hydrogen, forming a new copper compound with the structure CuR , in which R is the negative radical of the sulphuric acid.

What has become of the positive hydrogen? It was not incorporated in the copper compound, and it was not set free, else hydrogen would have been given off when the copper oxide and sulphuric acid were mixed. It must therefore have combined with the oxygen of the copper oxide molecule.

Our data justify the following graph:



The electrolysis of this and many similar compounds shows that metallic elements may replace one or more of the positive hydrogen atoms of acids, becoming themselves electrically positive.

This was illustrated in Experiment 34: $Mg + 2HCl = MgCl_2 + H_2$.

123. Electrolysis of Alkali and Alkali-Earth Compounds.—The deduction made in section 122, that metallic elements in combination are electrically positive, should be

confirmed by the electrolysis of two or three familiar compounds.

EXPERIMENT 52. *Electrolysis of Common Salt, NaCl.*-- Dissolve about 2 gm. of salt in 200 cc. of distilled water, add 2 or 3 cc. of phenolphthalein* solution and electrolyze in the usual manner. On passing the current, the contents of tube Y (Fig. 13) will assume a brilliant rose color, hydrogen will collect in the upper part of the tube, and chlorine will be set free and remain dissolved in the water of tube X, showing that the chlorine is electrically negative. Did the sodium migrate to tube Y? It has already been pointed out (p. 135) that sodium reacts upon water, forming an alkaline solution and liberating hydrogen simultaneously.

This experiment shows that the second hypothesis given on page 153 was correct, i.e., that the sodium migrated with the current into the tube Y. The results confirm the statement already made, that the metallic elements which combine with the acids take on positive electrical properties. This inference should be confirmed by electrolyzing solutions of potassium bromide, calcium chloride, and magnesium sulphate. Do the results suggest the possibility of such compounds as $\text{Ca}(\text{OH})_2$, and $\text{Mg}(\text{OH})_2$?

THE REACTION BETWEEN ACIDS AND ALKALIS

124. Neutralization.—The relations of the alkaline hydroxides to the hydroxides of the non-metals may be made clear by the following experiments:

EXPERIMENT 53. Put about 2 cc. of sodium hydroxide into an evaporating dish, and add dilute sulphuric acid, drop by drop, until the resulting solution will change the color of neither

* A solution of phenolphthalein is prepared by dissolving about .5 gm. of the powdered substance in 100 cc. of 95 per cent alcohol. It is changed to a rose-red color by alkaline solutions, while acids do not affect it. A solution of litmus may be substituted for it.

red nor blue litmus. Evaporate the solution to dryness and examine the product. Is it homogeneous? Does it possess the attributes of either constituent? Reserve a portion for further study, dissolve the remainder in water and electrolyze in the usual manner, using phenolphthalein or litmus as a coloring agent.

Treat a solution of potassium hydroxide with sulphuric acid as above directed. These tests show that an acid possesses the power to nullify or destroy the alkaline properties of an alkaline hydroxide. At the same time the acid loses its characteristic properties. This reaction is commonly spoken of as *neutralization*, and the resulting substance is said to be *neutral*. We have therefore three types of reaction shown by litmus: (1) Acid reaction, when blue litmus is reddened. (2) Alkaline reaction, when red litmus is made blue. (3) Neutral reaction, when neither variety is changed.

There are three corresponding types of solutions: (1) acid, (2) alkaline, and (3) neutral. We have here the somewhat anomalous fact that two types of hydroxides, prepared by the same process and dissolved in the same solvent, possess directly opposite chemical natures, for each can neutralize the power of the other. To understand this we need to know the changes within the molecule by which this transformation is brought about.

A better insight into the cause of neutralization may be had by ascertaining the amount of alkali which is required to neutralize a known weight of acid.

This may be done by treating a measured quantity of an acid whose strength is known, with an alkali solution of known strength, until the mixture is made neutral. The process is well illustrated when a measured quantity of oxalic acid solution (which contains 4.5 gm. of the acid dissolved in 1,000 cc. of water) is neutralized by a solution of sodium hydroxide (which contains 4 gm. of the hydroxide dissolved in 1,000 cc.

of water). These two solutions should be prepared by the instructor (see Appendix).

EXPERIMENT 54. Use the apparatus in Fig. 46. A and B are burettes (see Appendix) which are graduated to tenths of a cubic centimeter. They are equipped with brass pinchcocks or glass stopcocks, C D. If brass pinchcocks are used, the glass points E F are fastened to A B by short pieces of rubber tubing.

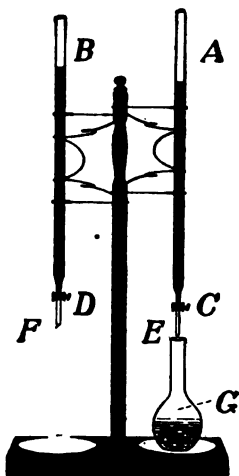


FIGURE 46

Fill tube A completely with the oxalic acid solution. Open the stopcock and let a few drops run out until all air is expelled from the rubber connection and from the glass point E. Fill tube B with the solution of sodium hydroxide. Now run into the flask G exactly 20 cc. of the acid solution, dilute it with from 20 to 30 cc. of distilled water, add 15 or 20 drops of phenolphthalein (0.50 gm. in 100 cc. of 95 per cent alcohol), and allow the sodium hydroxide to run in drop by drop until a rose color appears which remains upon shaking. This process of neutralizing is commonly called "titration." Repeat the titrations until constant results are obtained. The following values were taken from a student's note book:

	VOL. ACID	VOL. ALKALI
1.	20 cc.	19.7 cc.
2.	20 cc.	19.9 cc.
3.	20 cc.	19.9 cc.
4.	20 cc.	20.1 cc.

This shows that the oxalic acid in 20 cc. of the above solution was neutralized by the sodium hydroxide in about 20 cc.

of its solution. The weight of the acid and of the alkali used may be obtained as follows:

Acid . . 4.5 : 1000 :: X : 20 $\therefore$ X = 0.09 gm., = wt. of acid in 20cc.

Alkali . 4.0 : 1000 :: X : 20 $\therefore$ X = 0.08 gm., = wt. of alkali in 20cc.

It thus appears that 0.09 gm. of oxalic acid were neutralized by 0.08 gm. of sodium hydroxide. We wish to answer two fundamental questions:

1. In what *proportion* did the molecules react?

2. What was the result of the reaction?

(1) If that they reacted molecule for molecule, we should have the following proportion:

Mol. Wt.		Mol. Wt.		Wt. of		Wt. of
oxalic acid		sodium hydroxide		acid		alkali
90	:	40	::	0.09	:	0.08

Equating, we should have $0.09 \times 40 = 0.08 \times 90$, or $0.36 = 0.72$, which is not true.

The molecules then did not react in the proportion, 1 : 1. If, however, we multiply the molecular weight of sodium hydroxide by 2, we get a true proportion. This shows that one molecule of oxalic acid was reacted upon by two molecules of the sodium hydroxide.

(2) What was formed by this reaction?

This may be determined in the following manner: Thoroughly clean, dry and accurately weigh an evaporating dish about 7 cm. in diameter. Introduce 20 cc. of the acid and 20 cc. of the alkali (these are the proportions in which they are neutralized) into the weighed dish, evaporate the solution to dryness on a water bath, transfer it to a 100° drier, and heat until it is constant in weight.

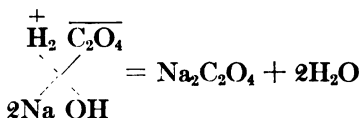
EXAMPLE.—Suppose dish and residue weigh 50.2680 gm.

“ “ weighs 50.1340 gm.

Weight of residue 0.1340 gm.

We may conjecture the reaction, but may be guided in this conjecture by the fundamental structures of the reacting compounds.

It was pointed out on page 157 that metallic elements replace the positive hydrogen of the acids, and presumably combine with the negative radical. Let this be the hypothesis. Since two molecules of NaOH react upon one molecule of $\text{H}_2\text{C}_2\text{O}_4$, we have;



If this is a true hypothesis, it follows that 90 parts of oxalic acid will yield 134 parts of the new substance, for

$\text{H}_2\text{C}_2\text{O}_4$		$\text{Na}_2\text{C}_2\text{O}_4$			
Mol. Wt. of Acid.	Mol. Wt. of Solid.	Wt. of Acid.	Wt. of Solid.		
90	:	134	::	0.09 gm.	: X
				$90 \text{ X} = 134 \times 0.09$	
				$\text{X} = 0.134 \text{ gm.}$	

In this case the theoretical and experimental weights, 0.134 gm., are identical. What does this signify?

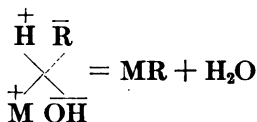
The process should be repeated, using solutions of hydrochloric and sulphuric acid which contain respectively 3.6 gm. and 4.9 gm. of the acid, dissolved in 1,000 cc. of water. Do the results confirm the theory that the sodium in the sodium hydroxide combined with the negative radical of the acid?

125. A General Formula for Neutralization.—Neutralization in these instances was effected by replacing the positive hydrogen of the acid with the positive metallic element of the alkali hydroxide. A general expression for neutralization of an acid by an alkali hydroxide is as follows:

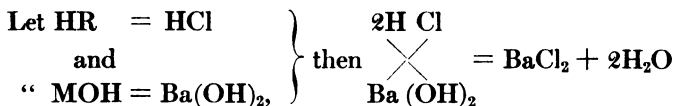
HR = general formula for an acid, in which R is an element or a group of elements acting as a negative radical.

MOH = general formula for a hydroxide, in which M is a metal or a group of elements acting as a positive radical.

Then the process of neutralization may be expressed by the graph,



In this general expression valence is not taken into account. It is meant to express only the general nature of the reaction. The formula may be applied to a specific reaction by considering the respective valences of the participating radicals. For example,



The compound resulting from the union of the positive metallic element of the alkali hydroxide, and the negative element (or radical) of an acid, during neutralization, is called a *salt*.

126. Neutralization, and Acids, Bases, and Salts.—

Acids, bases, and salts are three types of compounds, for which the following general expressions may be used:

1. HR , for any acid.
2. MOH , for any alkaline hydroxide.
3. MR , for any salt which results from their neutralization.

From the method of its formation, a salt, MR , may be viewed in two ways:

1. It is a positive metallic element combined with the negative radical of an acid.

2. It is an acid in which the positive hydrogen has been replaced by a metallic element. Either statement is consistent with the general process of neutralization already deduced.

127. The Naming of Acids, Bases, and Salts.—The system of naming acids, bases, and salts is comparatively simple.

I. The name of a compound which is made up of *two elements* consists of two words. The first is the name of the element which appears first in the formula. The root of the second word is the root of the name of the element which stands second in the formula, but it is given the termination, *ide* or *id*. This termination always means that the compound has but two elements. Thus:

CuO = Copper oxide.

HCl = Hydrogen chloride.

H_2S = Hydrogen sulphide.

MgCl_2 = Magnesium chloride.

HBr = Hydrogen bromide.

In the formulas and names of these and other similar compounds, the positive element always precedes the negative.

II. When an element forms acids (p. 151) whose molecules contain different amounts of oxygen, the root of the first word in the name of any of these acids is the root of the name of the element with a prefix or suffix which indicates the relative number of oxygen atoms in the molecule. The second word in the name is "acid." The first word in the name of the *most generally known* acid of an element, ends in *ic*. Acids of an element which contain more or less oxygen than the *ic* acid are named by changing the prefix or suffix to the root of the first word. Thus, when an acid contains more oxygen than the best-known *ic* acid, its name receives the prefix *per* and retains

the suffix *ic*; when one contains less oxygen than the *ous* acid of that element, its name receives the prefix *hypo* and retains the suffix *ous*. These principles of nomenclature are illustrated by the chlorine group of acids.

HClO_4 , perchloric acid.

HClO_3 , chloric acid.

HClO_2 , chlorous acid.

HClO , hypochlorous acid.

HCl , hydrogen chloride.

III. When the positive hydrogen of an acid is replaced by a metallic element (or a group of elements acting as a metal) to form a salt, the first word in the name of the salt is the name of the element which replaces the hydrogen, and the second is obtained by changing the suffix *ic*, to *ate*, and *ous* to *ite*; but the root of the first word in the name of the acid remains unchanged. Supposing these five chlorine acids to be neutralized with sodium hydroxide, we should have,

Perchloric acid yields sodium per-chlor-ate. . . . NaClO_4

Chloric acid yields sodium chlor-ate. NaClO_3

Chlorous acid yields sodium chlor-ite. NaClO_2

Hypochlorous acid yields sodium hypo-chlor-ite, NaClO

Hydrochloric acid yields sodium chlor-ide. . . . NaCl

IV. Acids are derived from the solution of non-metallic oxides in water. These oxides are therefore the acids without water. They have received the name *acid anhydrides*. Thus:

SO_2 is sulphurous acid anhydride, and $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$, sulphurous acid.

SO_3 is sulphuric acid anhydride, and $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$, sulphuric acid.

N_2O_5 is nitric acid anhydride, and $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$, nitric acid.

N_2O_3 is nitrous acid anhydride, and $\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HNO}_2$, nitrous acid.

EXERCISES

Name the following compounds:

1. CaCl_2 FeS C Cl_2 K_2CO_3 N_2O
2. CaSO_4 FeS_2 C Cl_4 H_2S N_2O_2
3. $\text{Ca}(\text{ClO}_3)_2$.. FeSO_3 CS_2 H_2O N_2O_3
4. $\text{Ca}(\text{ClO}_2)_2$.. FeSO_4 CH_4 H_2O_2 N_2O_4
5. $\text{Ca}(\text{ClO})_2$... FeCl_3 H_4C H_2S_2 N_2O_5
6. CaSO_3 FeCl_2 H_2CO_3 $\text{Mg}(\text{NO}_3)_2$.. KI

Write the formulas of the following substances:

Magnesium chlorate	Potassium sulphide
" sulphate	" sulphite
" carbonate	" sulphate
" chlorite	Phosphorus trioxide
" sulphite	" pentoxide
" sulphide	Sulphur dioxide
" hypochlorite	" trioxide
" hydroxide	" carbide
Potassium carbide	Sulphuric acid anhydride
" carbonate	Nitric " "
" chlorate	Nitrous " "
" hypochlorite	Sulphurous " "
" perchlorate	Carbonic " "

128. Substitution.—There is a third type of combination called *substitution*, which will be developed in the following pages.

EXPERIMENT 55. I. Weigh .25 gm. of pure silver, dissolve it in nitric acid as directed on page 92, and add sodium chloride in such quantity that there will be one molecule of salt for each atom of silver. By the principle demonstrated on page 51,

At. Wt. Ag	Mol. Wt. NaCl	Wt. of Ag	Wt. of NaCl
107	58.5	:: 0.25 gm. ::	X
.	107 X = 58.5 × 0.25		
	X = 0.1366 gm. salt required.		

II. This weighing may be readily accomplished in the following simple manner. Carefully dry about 3 gm. of pure salt as

directed on page 14, weigh about 2 gm. of it into a dry flask, and dissolve it in exactly 1,000 cc. of distilled water. Let it be supposed that 2.042 gm. was the amount dissolved. How many cc. of this solution will contain 0.1366 gm. of salt?

$$2.042 \text{ gm.} : 1,000 \text{ cc.} :: 0.1366 \text{ gm.} : X,$$

$$X = 66.8 \text{ cc., amount of salt required.}$$

III. Introduce exactly 66.8 cc. of the salt solution into the beaker, stir the mixture carefully, leaving the stirring rod in the beaker, and set it aside in a dark place for about 12 hours. (The white curdy precipitate which forms will be decomposed if it is long exposed to the light.)

Meanwhile prepare a weighed filter paper as directed in Experiment 35. Filter off the upper liquid through the weighed paper, and spray the precipitate with distilled water until the water which flows from the stem of the funnel does not redden blue litmus. Dilute the filtrate and washings to *exactly* 200 cc., and keep the solution for further study. Transfer the funnel with its paper to the 100° drier, and let it heat until it is apparently perfectly dry. Then transfer the paper with its contents to the reserved weighing bottle and heat again until constant in weight.

IV. The fact that a heavy white precipitate formed when the solutions were mixed is sufficient evidence that a chemical change was effected. We know also that the silver salt and the salt of sodium were present in the mixture, molecule for molecule. It does not follow, however, that they *reacted* in this proportion. That must be determined by the experiment.

EXAMPLE.—

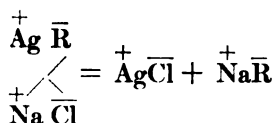
$$\text{Let weight of bottle} + \text{paper} + \text{ppt.} = 20.7949 \text{ gm.}$$

$$\text{Let weight of bottle} + \text{paper} \dots\dots\dots = 20.4620 \text{ gm.}$$

$$\text{Weight of ppt.} \dots\dots\dots = 0.3329 \text{ gm.}$$

We may assume a reaction, and ascertain if the data sus-

tain it. A study of the electrical properties of acids and salts suggests the following graph,



(Obviously the ascertained weight of the precipitate can be of no service in proving the truth of the graph, unless one of the hypothetical salts, AgCl or NaR, is wholly soluble, and the other wholly insoluble, in the given solution.) Test the insoluble salt (the precipitate obtained above) for AgCl, or some other compound of silver and chlorine (p. 94). Assuming that a chlorine salt of silver is found, the proportion in which the silver salt and the sodium salt combined may be determined. If they reacted molecule for molecule, one atom of silver formed one molecule of silver chloride, and we should have:

At. Wt. Ag	Mol. Wt. AgCl	Wt. of Ag	Wt. of AgCl
107	142.5	:: 0.25 gm.	X

$$107 X = 142.5 \times 0.25 \text{ and}$$

$$X = 0.3329 \text{ gm., the theoretical quantity of AgCl}$$

V. The fact that the theoretical weight for AgCl is the same as the experimental weight, and that this precipitate contains both chlorine and silver, leads to the conclusion that it is silver chloride.

It often happens in actual practice, that the theoretical and the experimental weights are not identical. This may lead to confusion. Here is a case in point. A student dissolved .107 gm. of silver, proceeded as above directed, and obtained 0.131 gm. of dried precipitate. It was shown that the precipitate contained both chlorine and silver. The theory gives;

At. Wt. Ag	Mol. Wt. AgCl	Wt. Ag	Wt. of solid
107	142.5	:: 0.107 gm.	X

$$107 X = 142.5 \times 0.107$$

$$X = 0.142.5 \text{ gm., the theoretical quantity of AgCl}$$

It is evident that the theoretical and the experimental results do not agree. Let it be supposed that two atoms of chlorine combined with one atom of silver. The theory gives,

At. Wt. of Ag	Mol. Wt. AgCl ₂	Wt. of Ag	Wt. of solid
107	: 178	:: 0.107	: X

$$107 X = 178 \times 0.107.$$

$$X = 0.178 \text{ gm., the theoretical quantity of AgCl}_2$$

Again, suppose two atoms of silver combined with one of chlorine:

Mol. Wt. Ag ₂	Mol. Wt. Ag ₂ Cl	Wt. of Ag	Wt. of solid
214	: 249.5	:: 0.107 gm.	: X

$$214 X = 249.5 \times 0.107$$

$$X = 0.124 \text{ gm., the theoretical quantity of Ag}_2\text{Cl}$$

It is apparent that the theoretical result will fall *below* 0.124 gm., if we *increase* the proportion of silver to chlorine; and that it will *exceed* .178 gm., if the proportion of chlorine to silver is *increased*.

The following table shows the various possibilities and relations:

TABLE IX

FORMULA	THEORETICAL WT.	ACTUAL WT.	DIFFERENCE
Ag Cl ₂	0.218 gm.	0.181 gm.	.082 + gm.
Ag Cl ₂	0.178 "	0.131 "	.047 + "
Ag Cl.....	0.142 "	0.131 "	.011 + "
Ag ₂ Cl.....	0.124 "	0.131 "	.007 - "
Ag ₂ Cl.....	0.118 "	0.131 "	.016 - "

The experimental weight, 0.131 gm., is .011 gm. too small for AgCl, and .007 gm. too large for Ag₂Cl. Since the error is about the same for each hypothesis, it would be necessary to repeat the experiment before a conclusion could be reached.

VI. The disposition of the sodium must now be ascertained. Since one atom of silver combined with one atom of chlorine, one atom of sodium and one molecule of R were freed from their former combinations. If the sodium and R combined, one atom of sodium may have combined with one or more molecules of R, or, one molecule of R may have combined with more than one atom of sodium. If all the sodium set free combined with all the R set free, they combined atom for molecule, forming NaR.

To ascertain the combination of the sodium, introduce 100

cc. of the filtrate into a weighed dish and evaporate it to dryness on the water bath. Dry the residue at 100° until constant

EXAMPLE.—

If the weight of the residue in 100 cc. = 0.0992 gm., the weight of the residue in 200 cc. (the total amount) = 0.1984 gm.

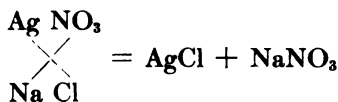
If the two radicals combined in a ratio of 1 : 1, the theory gives,

$$\begin{array}{l} \text{NaCl} \quad \text{NaR} \\ 58.5 : X :: 0.1366 \text{ gm.} : 0.1984 \text{ gm.} \\ X = 85, \text{ Mol. Wt. of NaR} \end{array}$$

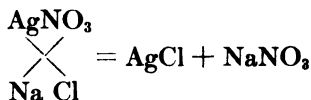
Now R = NO_3 , the negative radical of nitric acid. Hence we have,

$$\begin{array}{ccccccc} \text{Mol. Wt. NaCl} & & \text{Mol. Wt. NaNO}_3 & & \text{Wt. of NaCl} & & \text{Wt. of Solid} \\ 58.5 & : & 85 & :: & 0.1366 \text{ gm.} & : & 0.1984 \text{ gm.} \\ 58.5 \times 0.1984 & = & 85 \times 0.1366 & & & & \\ 11.6 + & = & 11.6 + & & & & \end{array}$$

Since this is a true proportion, it follows that one molecule of sodium nitrate was formed for each molecule of sodium chloride used. This gives authority for the graph,



The structure of R may be verified by mixing equi-molecular quantities of silver nitrate and sodium chloride and by proceeding as above directed. If the above interpretation is correct there will result,



Hence, wt. of precipitate : wt. of silver nitrate :: 142.5 : 170.
Or, wt. of AgNO_3 : wt. of NaNO_3 :: 170 : 85.

Do the experimental results confirm the deduction?

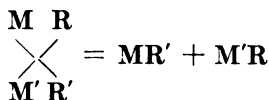
This graph represents a very broad range of chemical action, which may be formulated in a general expression. It was shown on page 163 that MR is the general form of a salt. Any other salt, not identical with MR , could be expressed by $M'R'$.

EXAMPLE.—

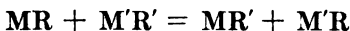
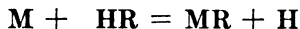
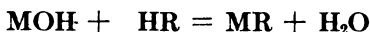
Let $Ag = M$, and $NO_3 = R$

“ $Na = M'$, “ $Cl = R'$

We would then have



as a general expression of the third method of forming salts. The three methods may be typified by three general formulas:



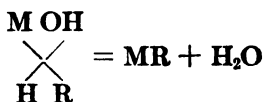
129. Bases and Hydroxides Compared.—It is apparent from the above equations that the metallic element M , which constitutes the positive radical of the salt, in each case existed originally (1) as an hydroxide, (2) as an element, or (3) in a salt. When such an element is combined with the negative of an acid, it is spoken of as *the base*. This term has a very broad and loose application. The alkaline hydroxides are usually spoken of as bases, presumably because they possess such strong affinities for acids. An element or its hydroxide may be “potentially” a base, but it does not become one until it combines with the negative of an acid; at least this is one interpretation to be placed upon the term base.

The three general expressions given on page 171 point clearly to the deduction that the hydroxides of the non-metals, and the alkaline hydroxides are fundamentally different. The placing of the oxygen and the hydrogen in the two types is wholly different. For this reason both types are not usually spoken of as hydroxides. The first are spoken of as the *acids*, while the second retain the term *hydroxides*, or *hydrates*.

Summary.—1. It has been developed in the preceding pages that acids (i.e., the hydroxides of the non-metals) and the alkaline hydroxides possess essentially different properties. The general structure of the acids may be expressed by the graph HR, that of the bases by the graph MOH.

2. Acids and the alkaline hydroxides possess the power to neutralize each other.

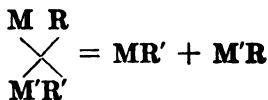
3. Neutralization consists in substituting or replacing the positive hydrogen of the acid, by a metallic element or a group of elements, as shown by the graph,



4. This gives three general types of compounds:

HR, the general type of an acid,
 MOH, the “ “ “ a hydroxide,
 MR, “ “ “ “ “ salt.

5. Another type of substitution occurs in the precipitation of one salt by another, for which the following general expression may be written:



EXERCISES

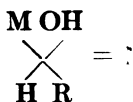
1. What evidence is there that water combines with the oxides of phosphorus, carbon, and sulphur, forming chemical compounds?
2. Is the solution of calcium oxide in water a chemical change? Why?
3. What effect would water have upon metallic calcium?
4. Iron dissolves readily in dilute hydrochloric acid. How could it be shown that the resulting compound does not contain positive hydrogen?
5. Define neutralization.
6. How many gm. of sodium hydroxide will be required to neutralize 4.5 gm. of oxalic acid? How many gm. of water would be given off?
7. In what proportion by weight must sodium hydroxide and hydrochloric acid be mixed to form a neutral mixture?
8. 25 cc. of HCl (3.65 gm. per 1,000 cc.) neutralized 100 cc. of potassium hydroxide; how many gm. in the 100 cc.?
9. Acetic acid has the formula $\overset{+}{\text{H}} \overline{\text{C}_2\text{H}_3\text{O}_2}$. How many gm. of it will be neutralized by 4.0 gm. of sodium hydroxide?
10. Vinegar is a weak solution of acetic acid. How could you determine the per cent of acid in a sample of it?
11. How could it be shown that potassium bromide precipitates silver bromide, AgBr, from a solution of silver nitrate?

The three general expressions given clearly to the deduction that the hydroxide and the alkaline hydroxides are fundamental placing of the oxygen and the hydrogen in different. For this reason both types of as hydroxides. The first are spoken of second retain the term *hydroxides*, or

Summary.—1. It has been developed pages that acids (i.e., the hydroxide the alkaline hydroxides possess essentially. The general structure of the acids graph HR, that of the bases by the

2. Acids and the alkaline hydroxides neutralize each other.

3. Neutralization consists in the positive hydrogen of the acid, by the of elements, as shown by the graph



4. This gives three general

HR, the general
MOH, the
MR, “

5. Another type of chemical reaction; but it may be another, but as heat, electricity, or magnetism. The time is dissolved by the sulphuric hydrogen. If the temperature of the and after a period of activity, it will be

duced may be transformed into which case the act to lift pieces of transformed into light will become luminous. transformed into electricity, or light. If energy of be derived from other must have existed origi-

Similar action was brought was shown that hydrogen flame. The energy which have been contained in some elements, hydrogen and oxygen. Good energy of elements is called *energy content*. Chemical energy heat, electricity, magnetism, etc., etc. Thus two elements may react hydrogen and chlorine. Others unite e.g., nitrogen and hydrogen. This *chemical affinity*. Usually when the action must be started by some heat, electricity, or light. Thus in hydrogen and the chlorine combined only if a lighted match, or in direct sunlight. as in oxygen with great brilliancy (see the phosphorus must be first ignited, but as by itself. What sustains the action? If energy of energy content, chemical action will be the dissipation or absorption of heat, electricity, or energy. In those chemical actions which heat or other energy is always given off, r

CHAPTER X

THE CONSERVATION OF ENERGY IN CHEMICAL REACTIONS

In an equation, the sum of the atoms on the right of the equality sign is equal to the sum of the atoms on the left. This follows from the law of the indestructibility of matter. The theory of the conservation of energy was first announced by Mayer in 1842, and asserts that energy cannot be created or destroyed, but only transferred or transformed.

130. Energy Defined.—By energy is meant the capacity to do work. For example, when one marble strikes another it expends energy which drives the second marble from its place. The energy of the first marble is lost to it, but is transferred to the second. It has been clearly demonstrated by physicists that the loss in energy which is sustained by any body when it does work, is acquired in the same proportion by the body which is acted upon. The newly acquired energy may manifest itself as motion, heat, light, electricity, or magnetism. Whatever its form, it is, in the aggregate, always equal to the original energy of the acting body.

131. Energy Transformed.—It seems that energy is either absorbed or dissipated in a chemical reaction; but it may become latent, or manifest itself as heat, electricity, or magnetism. This is illustrated in an electrical cell which is made from zinc and sulphuric acid. The zinc is dissolved by the sulphuric acid with the evolution of hydrogen. If the temperature of the cell be taken both before and after a period of activity, it will be

observed to have risen. The electricity produced may be transformed into magnetism in an electro-magnet, in which case the energy shows itself in the ability of the magnet to lift pieces of iron; or the energy of the current may be transformed into light by being passed through a fine wire, which will become luminous. Thus the chemical energy of the cell is transformed into electricity, magnetism, mechanical work, heat, or light. If energy of any kind cannot be created, but must be derived from other forms of energy, the energy of the cell must have existed originally in the zinc and sulphuric acid.

132. Selective Energy.—A similar action was brought out in Experiment 6, in which it was shown that hydrogen burns in oxygen with a very hot flame. The energy which here shows itself as heat must have been contained in some other form in the participating elements, hydrogen and oxygen. This special and poorly understood energy of elements is commonly called *chemical energy*, or *energy content*. Chemical energy differs from other forms, i.e., heat, electricity, magnetism, etc., in possessing a *selective* action. Thus two elements may react with great energy, e.g., hydrogen and chlorine. Others unite with difficulty or not at all, e.g., nitrogen and hydrogen. This selective energy is called *chemical affinity*. Usually when combination takes place, the action must be started by some outside force, such as heat, electricity, or light. Thus in Experiment 25, the hydrogen and the chlorine combined only upon the application of a lighted match, or in direct sunlight.

Phosphorus burns in oxygen with great brilliancy (see Experiment 38). The phosphorus must be first ignited, but the burning proceeds by itself. What sustains the action? If we accept the theory of energy content, chemical action will be accompanied by the dissipation or absorption of heat, electricity, or some other form of energy. In those chemical actions which proceed unaided, heat or other energy is always given off, and

the action is sustained at the expense of the chemical energy of the acting elements. Thus the union of hydrogen and oxygen may be *started* by an electric spark, but it must be *sustained* by the chemical energy of the participating elements. It is a fact of daily observation that the combustion of carbon in oxygen is accompanied by light and heat. Hence the molecule of carbon dioxide, which is the product of this combustion, must have less energy than the combining carbon and oxygen had.

On the other hand, hydrogen and iodine do not unite directly to form hydrogen iodide. After the union of these elements is started, it is not sustained by the chemical energy of the hydrogen and iodine. On the contrary, heat is *absorbed* when these two elements combine. The molecule of hydrogen iodide therefore contains more energy than was possessed by the combining elements. Hydrogen iodide and carbon dioxide represent two important classes of substances, one of which contains more energy than its elements, and the other less.

133. Energy in Molecules.—When a molecule contains *more* energy than its elements, it is said to be *endothermic*; when it contains *less*, it is said to be *exothermic*. The chemical affinity of the elements in endothermic compounds is slight, since to effect their union energy must be absorbed. These compounds are therefore conservers or storehouses of energy. The chemical affinity of the elements in exothermic compounds on the other hand, is strong. Their union, once started, often proceeds with great energy. The formation of exothermic compounds results in the transformation of chemical energy into mechanical energy, which can be made to do work.

The ordinary chemical equation does not therefore express the whole truth. Thus, when hydrogen burns in chlorine, heat and light are given off. We usually express the action by the graph, $H + Cl = HCl$. This accounts only for the atoms,

not for the energy. The amount of heat given off depends upon the quantity of material in action. Obviously we must adopt some standard in terms of which to interpret the amount of the energy. If we always consider the amount of heat which will be given off by the molecular weight in grams of the participating elements, we shall bring all equations to the same standard, as shown in Tables X and XI.

TABLE X

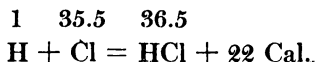
1 gm. of H	+	35.5 gm. of Cl	=	36.5 gm. of HCl
14 " " N	+	3 " " H	=	17 " " NH ₃
12 " " C	+	32 " " O	=	44 " " CO ₂
63 " " Cu	+	16 " " O	=	79 " " CuO

TABLE XI

Mol. Wt.	HCl 36.5	...NH ₃ 17	 CO ₂ 44	 CuO 79
Grams of substance.	36.5	 17	 44	 79
Ratio of molecules..	1	 1	 1	 1

134. Energy Expressed.—Let us apply this standard to the interpretation of the heat relations in three well-known reactions:

1. When 1 gm. of hydrogen combines with 35.5 gm. of chlorine to produce 36.5 gm. of hydrogen chloride, it is found that 22 calories* of heat are given off. Therefore

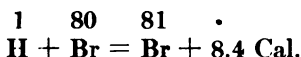


This graph accounts for both matter and energy.

2. When 1 gm. of hydrogen unites with 80 gm. of bromine

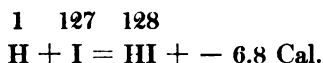
* A calorie is the amount of heat which will be required to raise the temperature of 1,000 cc. of water through 1°, e.g., from 14° to 15°.

to form 81 gm. of hydrogen bromide, 8.4 calories are given off. Hence we have,



3. It was pointed out on page 63 that iodine does not unite directly with hydrogen, and that when such a union is effected by indirect means, the product is an unstable gas which decomposes at ordinary temperatures.

It is found that the union of 1 gm. of hydrogen with 127 gm. of iodine not only does not liberate heat, but that it absorbs 6.8 calories. This may be expressed by the graph,



The minus sign before 6.8 means that this amount of heat was absorbed and became latent in the substance.

It is convenient therefore to adopt some plan of expressing both the conditions under which chemical action takes place, and the amount of heat which is absorbed or set free by such action. Usually chemical action takes place either (1) in a water solution of the acting elements, or (2) in a medium which is free from moisture.

1. When a compound dissolves in water with the evolution or absorption of heat, and the quantity of water is so large that an additional quantity of it will not alter the amount of heat which is thus absorbed or evolved, the action is expressed by adding the symbol Aq (a symbol for water) to the formula of the compound. Thus $\text{KCl}, \text{Aq} = -4.4$ means that 4.4 calories of heat are absorbed when 74.5 gm. (39 [at. wt. of K] + 35.5 [at. wt. of Cl] = 74.5) of potassium chloride are dissolved in a large volume of water. When the chemical reaction between elements takes place in a large volume of water, the

thermal action is expressed by separating the reacting elements by commas and adding Aq as before. Thus the heat set free during the formation of potassium chloride from the elements (when the combination takes place in a large volume of water) is expressed by the symbol K, Cl, Aq = 101.

2. If the elements unite directly in the absence of water, the action is indicated as above, except that the symbol Aq is omitted. Thus the combustion of hydrogen (1 gm.) in chlorine (35.5 gm.) is expressed by the graph, H, Cl = 22 Cal.

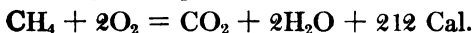
This method of expressing thermal changes is used in the following equations:

TABLE XII

1. Na, Cl = 97 Cal.	8. BaO, Aq = 27.8 Cal.
2. N, H ₂ = 11.8 "	9. SrO, Aq = 26.8 "
3. S, O ₂ = 71.0 "	10. SO ₂ , Aq = 7.7 "
4. SO ₂ , O = 32.1 "	11. SO ₃ , Aq = 39.1 "
5. Na ₂ O, Aq = 55.0 "	12. P ₂ , O ₅ = 363.8 "
6. K ₂ O, Aq = 65.4 "	13. P ₂ O ₅ , Aq = 41.6 "
7. CaO, Aq = 17.7 "	14. C, O ₂ = 97.0 "
15. CO ₂ , Aq = 5.6 Cal.	

These values, taken from data contributed by J. Thomsen, will throw additional light upon the equations which have been developed in the preceding chapters. It will be observed that all of the thermal values in these equations are positive. This seems to suggest that there is a tendency to form exothermic compounds. Were this reversed, spontaneous chemical action would be a refrigerating process. Carbon (coal) and marsh gas, CH₄, are the fuels of chief importance.

The following thermal values have been determined:



If these reactions were endothermic, then in the combustion of 12 gm. (at. wt. of C = 12) of carbon, 97 calories would

be absorbed. This means that the combustion of 1 lb. of coal (if it were pure carbon) would absorb sufficient heat to freeze about 30 liters of boiling water. During the combustion of 16 gm. (12 [at. wt. of C] + 4 [wt. of H_4] = 16) of marsh gas, 212 calories would become latent. This is equivalent to saying that the combustion of 500 liters of the gas, CH_4 , would absorb sufficient heat to freeze about 48 liters of boiling water.

Endothermic compounds, e.g., hydrogen iodide, contain more energy than the chemical energy of the participating elements. Since the tendency of chemical change is to liberate heat, we should expect to find endothermic compounds unstable. Such is the fact. Some of them will even decompose spontaneously—sometimes with explosive violence. This instability is well illustrated by the iodide of nitrogen, which may be easily prepared.

EXPERIMENT 56. *Caution! The product of this experiment is a powerful explosive.* Put about 0.5 gm. of iodine and 1 gm. of potassium iodide into a beaker, add 2 or 3 cc. of water, stir well until the iodine is about dissolved, add approximately 10 cc. of strong ammonia, and let the mixture stand in a quiet place until a brownish precipitate separates. Filter, divide the precipitate into three parts, place each part upon an unglazed brick or piece of filter paper, and put in separate parts of the room to dry. When dry it will explode upon being touched with a feather. Sometimes even the vibrations of the floor will cause an explosion.

THE SYNTHESIS OF ENDOTHERMIC COMPOUNDS

Notwithstanding their instability, endothermic compounds are produced in nature in great variety and abundance. Such familiar substances as starch, sugar, albumen, fat, wax, etc., belong to this class.

135. Photosynthesis.—This upbuilding of endothermic molecules is accomplished in nature primarily by the green tissue of plants. This may be better understood by examining the structure of a leaf. Fig. 47 is a cross section of a leaf; A is the epidermis on the lower surface and B is the epidermis on the upper surface. On the lower surface are numerous openings called stomata (Fig. 47, D), each of which is commonly bounded by two cells called guard cells. These stomata have the power, according to the conditions which surround the plant, of opening and closing. By this means the inner tissue of the leaf bearing the chlorophyll (green) granules (Fig. 47, C) may be

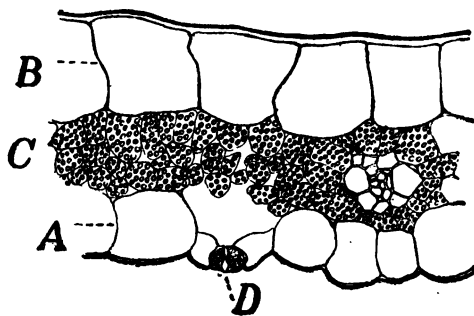


FIGURE 47

entirely cut off from the outside air, or it may, under other conditions, be in direct communication with the atmosphere outside. It is especially by the activity of these chlorophyll granules, to which the air is brought through the stomata, that endothermic compounds are built up. The surface of a leaf is surrounded by the air, which contains nitrogen, oxygen, carbon dioxide, and moisture. Nitrogen possesses little spontaneous action. Oxygen is a vigorous element, which of course contains chemical energy. The carbon dioxide and water are, as we have discovered, strong exothermic compounds. Chlorophyll possesses the remarkable power of building up starch, a strong endothermic compound, from carbon dioxide and water. The plant must obtain from the outside the energy which it puts into the starch molecule. This source of power is thought to be the sunlight, since no starch is formed without it. The

synthesis of the starch molecule may be expressed by the graph,

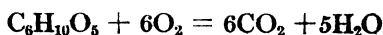


136. The Purpose of Photosynthesis.—The plant manufactures starch and sugar for its own food. A very considerable surplus is often formed, and this may be stored in some part of the plant, as in seeds. In this case it serves as food for the embryo during germination. Starch is also found in potatoes, wheat, corn, rye, barley, beans, etc. These serve as the raw materials from which our own starchy foods are derived. The presence of starch in various grains, etc., is shown in the following table:

TABLE XIII

	WATER	ALBUMEN	FAT	STARCH
Wheat.....	13.35.....	16.6.....	0.9.....	69.1
Rice.....	12.58.....	7.7.....	0.4.....	79.2
Barley.....	—.....	13.0.....	2.7.....	76.0
Corn.....	13.5.....	10.0.....	6.7.....	64.5
Potatoes.....	74.0.....	2.0.....	0.16.....	21.0

137. Endothermic Compounds, and Foods.—These and many other endothermic compounds are used for food. Some of them may be used directly, e.g., cereals, fruits, peas, beans, etc., while others must be transformed into eggs, milk, flesh, etc., by animals before they can be assimilated by the human species. These various articles of food are taken into the human body, where, in the processes of digestion and assimilation, they are slowly transformed into exothermic compounds by the oxygen which is supplied to the tissues through respiration. The final oxidation of starch within the body may be expressed by the graph,



During this process much energy is set free, and appears in the body as heat and muscular power. *Our foods are therefore power-producers and heat-producers because they are endothermic compounds.*

138. Stability of Exothermic and Endothermic Compounds.—In the formation of endothermic compounds through the activity of chlorophyll in sunlight, the radiant energy from the sun is stored up in unstable molecules. The fact that spontaneous action tends to form exothermic compounds enables us to draw upon endothermic molecules as storehouses of energy.

It is a direct corollary from the law of energy conservation that an exothermic compound can be decomposed into its elements only when the *same* quantity of energy that was given off in its formation is again restored to the participating elements. Thus 22 calories must be added to 36.5 gm. of hydrochloric acid (p. 177) to decompose it into hydrogen and chlorine. In general, the stability of a compound is *inversely proportional* to its energy content.

We now have before us two generalizations whose significance is far-reaching:

- (1. Acids, bases, and salts are made up of radicals which possess opposite electrical properties.)
2. The individual representatives of these three types possess unequal degrees of stability.

139. Electrolysis of Exothermic Compounds.—It will now be our purpose to inquire more specifically into the meaning of the electrical relations of these compounds. It was pointed out on page 150 that pure water is a very poor conductor of electricity, but that it becomes a conductor when it contains an acid or an alkaline hydroxide in solution. It was shown in addition (page 158) that common salt, calcium chlo-

ride, copper sulphate, etc., in solution, also make water a conductor. This was interpreted to mean that these compounds contain electrical units of opposite character. The question arises, why is it that during electrolysis these positive and negative radicals migrate to the opposite electrodes? All we know is that they possess inherently opposite electrical properties, and transport these opposite charges of electricity through the liquid to the electrodes.

140. Dissociation.—It has also been pointed out that the dilute solutions of acids, bases, or salts are generally good conductors. Now a molecule, e.g., sodium chloride, cannot conduct an electric current until it has been separated into its radicals, Na and Cl. These elements are combined with considerable chemical force and, according to the law of conservation of energy, it will require an equal amount of force to tear them asunder. Since the electric current is apparently the only active force brought to bear on the solution, it would appear that the requisite amount of energy to decompose the molecule must be drawn from it. This would seem to mean that a very considerable portion of the passing current would be used up in the cell itself; but this is not the case. There is a theory to explain why the electricity is not used up in the cell, namely, that in many dilute solutions, *molecules* of the substance put into the solvent do not exist; *they have been separated into their positive and negative radicals*. Observations of the influence of these compounds on the freezing point of various solvents support the theory.

It was pointed out on page 128 that $\text{Mol. Wt.} = \frac{C}{\text{Sp. Dep.}}$
 in which C is a constant for each solvent. The numerical value of C is about 18.5 when water is the solvent. Hence

$$\text{Mol. Wt.} = \frac{18.5}{\text{Sp. Dep.}}$$

The following analyses by Meyer are suggestive:

TABLE XIV

A SUBSTANCE	B 1 GM. IN 100 CG.	C DEPRES- SION.	D MOL. WT. (M.) = $\frac{18.5}{\text{SP. DEP.}}$	E KNOWN ML. WT.
Sodium chloride	58.40	0.600°	$M = \frac{18.5}{0.6} = 30+$	58.4
Potassium chloride . .	74.40	0.446°	$M = \frac{18.5}{0.446} = 41+$	74.4
Ammonium chloride .	53.40	0.653°	$M = \frac{18.5}{0.653} = 28+$	53.4
Potassium bromide . .	118.80	0.292°	$M = \frac{18.5}{0.292} = 63+$	118.8
Potassium iodide . . .	165.60	0.212°	$M = \frac{18.5}{0.212} = 87+$	165.6
Magnesium sulphate.	245.9	0.072°	$M = \frac{18.5}{0.072} = 256+$	245.9
Nickel sulphate	280.1	0.055°	$M = \frac{18.5}{0.055} = 336+$	280.1
Copper sulphate	248.8	0.065°	$M = \frac{18.5}{0.065} = 284+$	248.8

It will be observed that the calculated molecular weight of the first five compounds (column D) is approximately one-half of the accepted molecular weight which has been determined by other methods. The calculated weights of the succeeding sulphates approximate their known respective molecular weights. This is interpreted to mean that the molecules of the first five compounds do not exist unchanged in the dilute solutions, but that they have been dissociated into their positive and negative radicals, e.g., $\text{Na}^+ \longleftrightarrow \overline{\text{Cl}}$, thereby doubling the number of units in the solution. The deportment of the three sulphates is construed to mean that they are not dissociated readily in dilute solutions, and hence the number of individual

units is not doubled. This theory is strengthened by the investigations of Arrhenius, Ostwald, and others.

Radicals thus dissociated are called *ions*, and the process of dissociation is called *ionization*. Ionization is found to be especially active in dilute solutions of the alkali salts of the mineral acids. The percentages of some compounds which undergo dissociation in dilute solution, is shown in the appended table.

TABLE OF DISSOCIATION. XV. (Meyer)

SUBSTANCE	STRENGTH OF THE SOLUTION	PER CENT OF DISSOCIATION
Sodium hydroxide	40 gm. in 1000 cc. water	73
Potassium hydroxide . . .	56 " " " "	77
Potassium chloride	79 " " " "	75
Hydrochloric acid	36 " " " "	78
Nitric acid	63 " " " "	82
Potassium nitrate	101 " " " "	64
Sulphuric acid	98 " " " "	51
Potassium sulphate	174 " " " "	53

141. Dissociation, and the Theory of Electrolysis.—

A number of important deductions may be made from the preceding facts:

1. The molecules of an electrolyte (a compound which makes water a conductor of electricity) are split up into ions, but not by the electric current.

2. Ions are electrically charged atoms or groups of atoms.

3. The electricity passes through the solution because the ions transport it.

4. When the electric current passes into a solution containing ions, those which are positively electrified separate from those which carry a negative charge.

5. When the oppositely charged ions reach the electrodes,

they give up their electricity to the electrodes, which are composed of a good conductor.

6. An atom which is charged with electricity possesses very different attributes from the same atom when it is not so charged. Thus, when sodium chloride is dissolved in a large quantity of water, it dissociates into Na and Cl. The sodium does not react with the water, and the chlorine does not escape. When, however, they give up their electrical charges, as they do during the electrolysis of salt, each element assumes its normal attributes.

Summary.—The fundamental principles which have been discussed in the preceding chapters, and in some measure elucidated, may be grouped under the following heads:

1. The theoretical limit to which matter may be divided is the atom.

2. The atomic theory of matter is a reasonable working hypothesis.

3. Atoms possess all of the essential properties of matter.

4. $\text{Density} = \frac{\text{mass}}{\text{volume}}.$

5. The number which expresses the density of a gas is one-half its molecular weight.

6. Like volumes of all gases, under like conditions of temperature and pressure, contain the same number of molecules.

7. Atoms always combine in definite proportions.

8. The gross weights in which atoms enter into combination are directly proportional to the atomic weights of the respective atoms, or some multiple thereof.

9. Valence is a variable function of atoms.

10. The oxides of the non-metals, when dissolved in water, usually form acids, while the oxides of the metals form hydroxides.

11. The general type of an acid is HR; of an hydroxide, MOH.

12. Neutralization consists in replacing the positive hydrogen of an acid by the positive metal of a hydroxide. This forms a salt.

13. A chemical reaction is usually attended by the absorption or dissipation of energy.

14. When certain salts are dissolved in water, they dissociate into their positive and negative ions.

EXERCISES

1. Why does the rubbing of a match against a rough surface strike a blaze?

2. Why does a meteor glow when it passes through the earth's atmosphere?

3. Will it require more heat to change a pound of ice at 0° , or a pound of water at 0° , into boiling water? Why?

4. Why is it that a comparatively large volume of water, whose temperature is near 0° , will be kept at that temperature by a small piece of ice, when the temperature of the surrounding air is much warmer?

5. Will a pound of steam at 100° contain more or less heat than a pound of boiling water? Why?

6. When steam is condensed to water, it always heats the condenser. Why?

7. Would the steam which leaves the cylinder of a locomotive be hotter or colder than when it enters?

8. When pure water is boiled in an open vessel, the temperature does not rise above 100° . What becomes of the heat which it absorbs, after its own temperature has been raised to 100° ?

9. How many calories of heat will be required to raise the temperature of 15 liters of water from 14° to 15° ? Is it likely that 15 liters of mercury will require the same amount of heat?

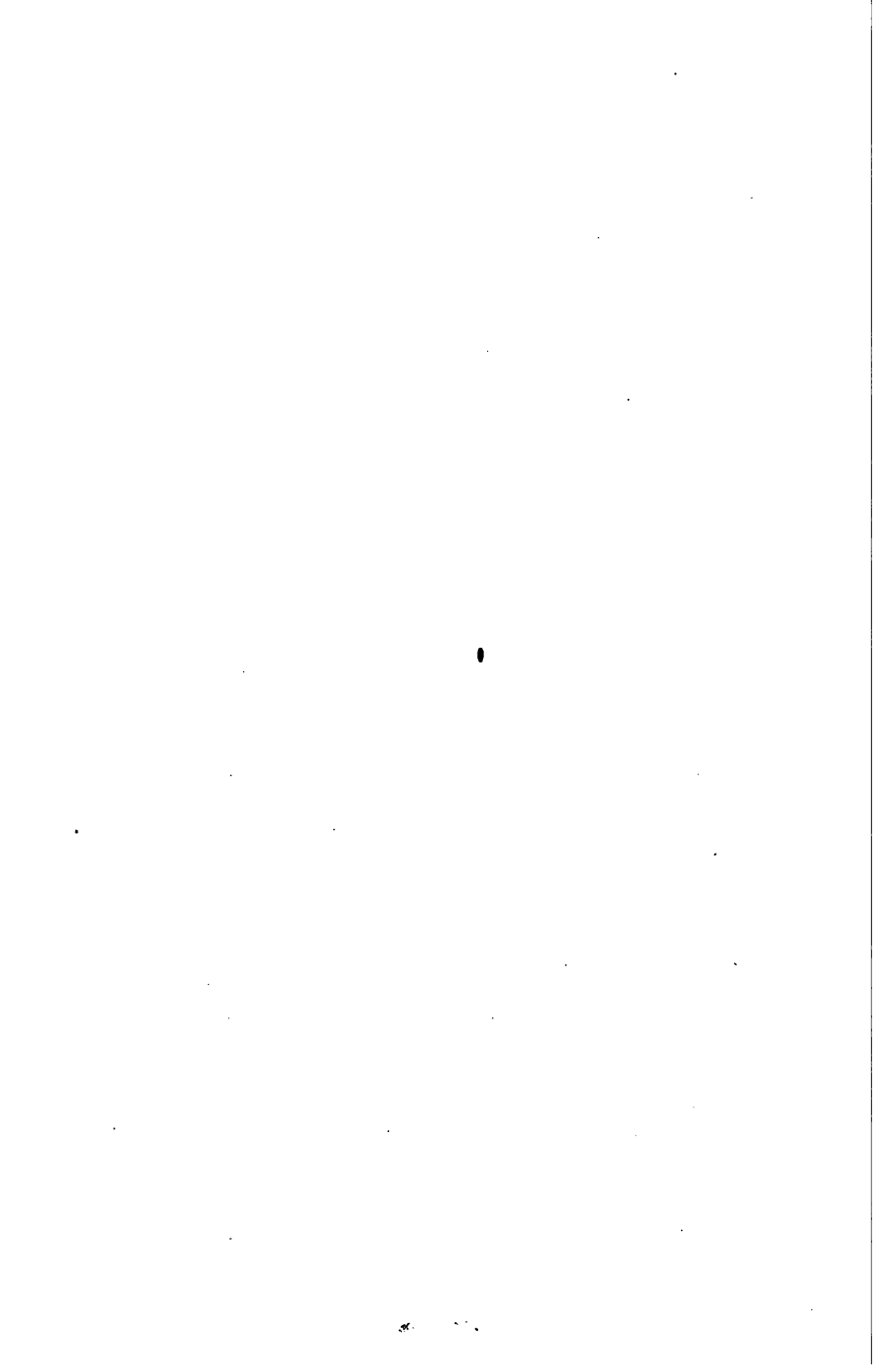
10. Interpret the expression, $H, Cl = 22 \text{ Cal.}$

11. Interpret, $H, Cl, Aq = 39 \text{ Cal.}$

12. Which of the following is endothermic, $A, B = 16 \text{ Cal.}$, or $A', B' = -16 \text{ Cal.}$?

PART II

The student should now have a clear notion of formulas, and the significance of an equation. Equations not determined by the student will be used freely in what follows. These equations may be accepted, because they have been carefully determined by chemists. The general laws of chemistry, which have been developed in the preceding chapters, will be used in discussing many important industrial processes. Indeed, the discussion of these industrial processes will show to what extent the laws of chemistry are used, and the contribution which they make to the breadth and comfort of our daily life. It is also proposed to examine each of the important elements in detail and to discover its true position in the great series of chemical elements upon whose constant activity all life depends. The student is asked to accept the statement (to be demonstrated later) that the grouping of the elements into families is based upon a great law, the interpretation of which is one of the achievements of modern chemistry.



CHAPTER XI

THE HALOGEN GROUP OF ELEMENTS: GROUP I.

This group includes chlorine, bromine, iodine, and fluorine. They are called *halogens* (salt producing), because they unite directly with metals and form compounds whose attributes are salt-like in character. These elements have similar chemical properties, and the physical and chemical properties of their corresponding derivatives are similar.

FLUORINE, F (At. Wt. 19)

142. This element is not found free in nature. Its most important compounds are calcium fluoride, CaF_2 , commonly called fluorspar, and cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$ (Al=aluminium), a mineral found in great abundance at one point in Greenland. Fluorine is also found in combination in the tissues of some plants, in bones, teeth, milk, blood, etc. It was first obtained in a comparatively pure state by Moisson in 1886, who electrolyzed, at -23° to -50° , pure hydrogen fluoride, HF, mixed with a little potassium fluoride, KF. The process was carried on in a platinum tube, because the hydrogen fluoride attacks glass with great energy.

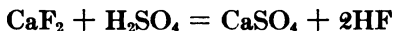
143. Properties.—Fluorine is a yellowish-green gas with an unpleasant, chlorine-like odor. It shows a powerful affinity for hydrogen, with which it unites explosively even in the dark. So great is the affinity of fluorine for hydrogen, that many compounds which contain hydrogen are spontaneously decomposed on being brought into contact with it. Thus wood, cork, paper, alcohol, and turpentine, all of which contain hydrogen, are ignited spontaneously, on contact with fluor-

ine. It is said that Moisson dropped some liquid fluorine upon a wooden floor, which immediately burst into flame.

COMPOUNDS OF FLUORINE

No oxygen compounds of this element are known.

144. Hydrofluoric Acid.—One atom of fluorine combines with one atom of hydrogen and forms hydrofluoric acid; but the acid is usually prepared by distilling a mixture of potassium or calcium fluoride, mixed with sufficient concentrated sulphuric acid to make a thin paste:



The escaping fumes of HF are passed through a cold platinum tube, in which they are condensed, and collected in vessels made of platinum, wax, or rubber. The commercial acid is usually prepared by conducting the gas (HF) into rubber vessels containing water. The commercial acid is therefore a solution of the acid, HF, in water.

Substances like glass, containing silicon dioxide, are readily disintegrated by hydrofluoric acid. This action is easily illustrated.

The Etching Process.—Caution! Very poisonous fumes are formed. Perform this experiment under the hood.

EXPERIMENT 57.—Having prepared a waxed glass plate as indicated below*, put about two gm. of calcium fluoride into a leaden crucible, moisten it with concentrated sulphuric acid, taking great care not to expose the hands or face to the fumes, and quickly cover the vessel with the glass plate, waxed side down.

The chemical effect of the fumes generated in the crucible, upon the glass (which is a mixture of silicates such as CaSiO_3), may be expressed by the graph,



The silicon tetrafluoride passes off as a vapor. The glass exposed to the fumes assumes a porcelain-like appearance.

*This plate may be prepared as follows: Place a few shavings of paraffin on a clean, dry glass plate, and hold it over a small flame until the paraffin is melted. Allow the liquefied paraffin to flow uniformly over the surface; then let it cool and solidify. Cut a design upon the waxed surface with the point of a knife-blade, in order to expose some part of the glass.

This property of hydrofluoric acid is utilized commercially for making the graduation marks upon the stems of thermometers, burettes, etc., and in etching delicate designs upon glass.

145. Salts of Hydrofluoric Acid.—This is a strong monobasic acid which neutralizes solutions of the alkali hydroxides, and combines with other basic oxides to form stable salts, most of which are not soluble in water.

CHLORINE, CL (AT. WT. 35.45)

146. The method of preparing chlorine and its properties were given in connection with Experiment 22 (p. 54). For the preparation and properties of hydrogen chloride, see Experiment 25 (p. 57).

147. Oxygen Derivatives of Chlorine.—Chlorine does not combine *directly* with oxygen. Union can be effected only in the presence of some basic oxide, especially the oxides (or hydroxides) of sodium, potassium, calcium, barium, etc. The resulting compound is a salt in which the oxide of chlorine plays the part of a *negative radical*:

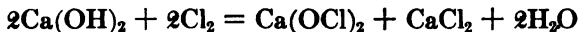


The oxides of chlorine which have been prepared and separated, have been obtained from these salts. Two oxides of chlorine are well known: Cl_2O , chlorine monoxide, and ClO_2 or Cl_2O_4 , chlorine dioxide.

Chlorine monoxide combines with water, forming hypochlorous acid: $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HOCl}$. It is therefore an acid anhydride.

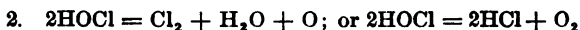
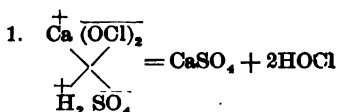
148. Salts of Hypochlorous Acid.—With strong bases, hypochlorous acid forms salts which are more stable than the free acid. Of these the most important is calcium hypo-

chlorite, $\text{Ca}(\text{OCl})_2$. This and other compounds are formed when chlorine acts upon powdered calcium hydroxide, and the mixture is called "bleaching powder." The chemical change is indicated by the equation,

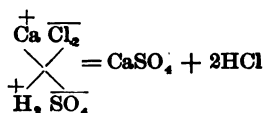


When bleaching powder is moistened with dilute sulphuric acid, a part of its chlorine is set free; and upon this its effectiveness in bleaching depends.

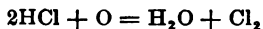
The chemical changes are not known with certainty. They are probably those represented by the following graphs;



The calcium chloride will also be acted upon by the sulphuric acid, liberating hydrochloric acid;



The nascent oxygen from the hypochlorous acid reacts upon the hydrochloric acid and forms water and chlorine;



149. Properties of Bleaching Powder.—Calcium hypochlorite is a convenient form in which to store chlorine. It is reasonably stable, it may be transported without loss, and it liberates its chlorine with great ease. It is therefore admirably adapted to commercial requirements. Its effectiveness in bleaching may be illustrated by the following experiment:

EXPERIMENT 58.—Shake up about 20 gm. of the powder with about 100 cc. of water, allow the mixture to settle, and carefully pour off the pure upper liquid. Moisten a piece of ordinary red

calico, a flower, or a piece of unbleached muslin with dilute sulphuric acid (1:20), and then place it in the clear liquid and let it remain for at least twelve hours. It will be found to have been completely decolorized.

150. Bleaching Cotton and Linen Fabrics.—The processes used in the bleaching of cotton are essentially the same as those used for bleaching other fabrics, such as linen and paper.

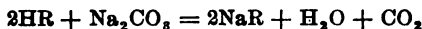
I. Cleansing.—The first step consists in boiling the cotton in water which contains considerable "milk of lime," $\text{Ca}(\text{OH})_2$, suspended in it. This changes the resin and fat compounds, which are normally present in the raw material, into insoluble calcium soaps.

II. Souring Process.—The cotton is then washed thoroughly with water to remove any soluble particles (such as any unused portion of $\text{Ca}(\text{OH})_2$). The calcium soap remains in the meshes of the fabric, and is removed by treatment with a dilute acid, such as hydrochloric or sulphuric. This is called the souring process. The fundamental action of the dilute acid may be represented by the graph,



This equation means that the calcium is transformed into the readily soluble calcium chloride, CaCl_2 , and an acid, HR, is set free. This acid, called a fatty acid, may or may not be soluble in water. Its removal, together with any remaining impurities, constitutes the next important step.

III. Washing with Soda-ash, Na_2CO_3 .—For 4,000 lbs. of cloth, about 150 lbs. of soda-ash, mixed with sufficient water to thoroughly cover the cloth, is used. An imperfectly soluble soap is formed with any fat which may remain in the cloth. This may be represented by the equation,

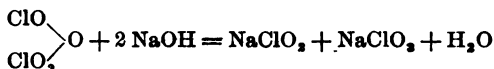


IV. Bleaching.—The soap, NaR, and other soluble impurities are then removed by careful washing and rinsing. The thoroughly cleaned fabric is then immersed in a clear solution of bleaching powder, which has enough of the powder to give it a specific gravity of about 1002.5. The solution is then treated with enough dilute hydrochloric or sulphuric acid to liberate hypochlorous acid, which decomposes spontaneously into chlorine and oxygen. The nascent chlorine and oxygen act upon the coloring compounds of the fabric, forming new substances which are without color. The bleached fabrics are then washed and dried.

151. Chlorine Dioxide, ClO_2 , or Cl_2O_4 .—This exceedingly explosive substance may be prepared by moistening a mixture of potassium chlorate and oxalic acid, with dilute sulphuric acid (1 : 2). When this mixture is heated gently (not to exceed 30°), a greenish-yellow gas is given off. This may be condensed by a freezing mixture to a reddish-brown liquid. It is exceedingly explosive when it is suddenly heated, or when it comes into contact with wood, cork, sugar, or other combustible substances.

152. Properties of Chlorine Dioxide.—It dissolves in water forming a yellow, acid liquid which possesses strong bleaching properties. Its density is 33.75, corresponding to the formula ClO_2 . There is considerable evidence that the molecule is doubled when the gas is liquefied or dissolved in water. Thus an alkali hydroxide, in neutralizing its aqueous solution, forms two classes of salts, the chlorites and the chlorates (p. 197).

This process may be expressed by the graph,



It therefore possesses the character of a mixed acid anhydride.

Chlorous acid, HClO_2 , and its anhydride, Cl_2O_3 , are unknown.

153. Chloric Acid, HClO_3 , is known only in its aqueous solution, and in combination with metals. Its aqueous solution may be evaporated in a vacuum until it contains about 40 per cent of pure acid. This solution is a powerful oxidizing agent. Such substances as alcohol, wood, phosphorus, and sulphur ignite spontaneously when dipped into it. It neutralizes the alkali hydroxides, and forms salts which are more stable than chloric acid. Chlorates are

readily formed by conducting chlorine into a *hot* solution of an alkaline hydroxide until it is saturated:



EXPERIMENT 59.—*Caution! Perform this experiment under the hood, and keep the windows closed to avoid draughts.* Dissolve 25 gm. of caustic potash in about 100 cc. of water, put the solution into a beaker, heat it nearly to boiling, and pass chlorine (prepared as in Experiment 22) into it until the liquid loses its alkaline reaction. The end of the delivery tube which conducts the chlorine into the caustic potash should terminate just below the surface of the liquid, otherwise its mouth will be quickly choked by the separating crystals.

Let the chlorinated solution stand several hours, drain off the upper liquid, dissolve the crystals in the least possible amount of boiling water, filter while hot (if the solution is not clean), and let stand until crystals separate from the filtrate. Drain off and dry the crystals. They may be identified in two ways:

(1). They give off oxygen when they are mixed with manganese dioxide and heated (p. 28.)

(2). When they are moistened with dilute sulphuric acid (1:2), chlorine dioxide is set free.

154. Salts of Chloric Acid.—Potassium chlorate is the best known and most important salt of chloric acid. It is used to a limited extent in medicine. Formerly it was used as an ingredient of certain explosives which were used in blasting. Its efficiency is due to the ease with which it gives off oxygen when it is struck sharply, or suddenly heated. These preparations are no longer used on a large scale, because they are so sensitive to shock that they cannot be transported with safety. They still find a limited use in the manufacture of torpedo caps which are placed upon railroad tracks for signals. These caps are made of potassium chlorate and powdered sulphur. The sudden pressure put upon them by the passing train liberates the oxygen, which oxidizes the sulphur to sulphur dioxide. The explosion is due to the sudden expansion which is produced by the newly formed gases.

155. Perchloric Acid, HClO_4 , is a colorless, caustic, and fuming liquid which dissolves readily in water. The concentrated solution is

much more stable than the corresponding solution of chloric acid. It is not decomposed by alcohol, paper, or other organic substances.

BROMINE, BR (AT. WT. 79.96)

156. Bromine, also, because of its exceptional activity, is not found free in nature. It is found in great abundance, in a combined form, in the salt deposits of Stassfurt, Germany. It also occurs in combination in sea-water to the extent of about 1 gr. per gallon, and certain mineral springs, especially those at Kreuznach, Germany, contain still more bromine in combination. Bromine has also been produced in large quantities from certain salt wells in the Kanawha Valley, in West Virginia. After the major portion of the salt has been crystallized out by evaporation, the remaining liquid, called the "mother liquor," is evaporated to near dryness and then heated with manganese dioxide and concentrated sulphuric acid, as outlined in Experiment 60.

157. Preparation of Bromine.—*Caution! Perform all experiments with bromine under the hood, keeping the windows closed.* Its vapor is a powerful caustic and irritant to the skin and mucous surfaces.

EXPERIMENT 60. Use the apparatus shown in Experiment 22. Mix thoroughly about 5 gm. of potassium bromide with an equal volume of manganese dioxide, introduce the mixture into the generator A, connect as before directed, run in about 10 cc. of concentrated sulphuric acid from C, apply a gentle heat to A, and bromine will distill over.

158. Properties of Bromine.—In its commercial form, bromine is a heavy, reddish-brown liquid with an exceedingly disagreeable odor, somewhat like that of chlorine. It is about 3.18 times as heavy as water. It is very volatile even at ordinary temperatures, forming dark brown vapors. It is more soluble in water than chlorine is, and it dissolves readily in alcohol, ether, chloroform, and carbon bisulphide. It is

strikingly like chlorine in its chemical properties, though somewhat less energetic.

COMPOUNDS OF BROMINE

159. Hydrogen Bromide, HBr, is formed when hydrogen burns in the vapor of bromine, or when potassium bromide is moistened with strong sulphuric acid. It is a colorless gas which fumes in the air, and dissolves readily in water to a colorless, acid fluid, usually called hydrobromic acid. This solution has essentially the same properties as a solution of hydrochloric acid.

160. Oxygen Derivatives.—There are three hypothetical oxides of bromine, Br_2O , Br_2O_5 , and Br_2O_7 , none of which has been prepared and isolated. These are regarded as anhydrides of hypobromous acid, HBrO , bromic acid, HBrO_3 , and perbromic acid, HBrO_4 . These acids have been prepared. Their salts, called respectively hypobromites, bromates, and perbromates, have, in general, properties similar to the corresponding salts of the chlorine acids.

IODINE, I (At. Wt. 126.85)

161. For the methods of preparation and properties of iodine and hydriodic acid, see page 62.

COMPOUNDS OF IODINE

162. Oxygen Derivatives.—Iodine Pentoxide, I_2O_5 , is the most important oxide of iodine which has been isolated. It is a white crystalline powder which dissolves in water, forming iodic acid: $\text{I}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HIO}_3$.

It is, therefore, iodic acid anhydride. It decomposes only at 300° , into iodine and oxygen, and so is the most stable of the halogen oxides. This is in harmony with their respective

heats of formation. The other halogen oxides are strong endothermic compounds, while the heat of formation of I_2O_5 from the elements is + 44.8 Cal. It is therefore strongly exothermic.

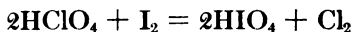
163. Iodic Acid.—The iodine compounds of hydrogen and oxygen corresponding to hypochlorous and chlorous acid are unknown. The first member of the series whose properties are well known is iodic acid. It may be prepared by dissolving its anhydride, I_2O_5 , in water; or by the action of strong nitric acid upon iodine crystals. It is also formed by the action of iodine upon chloric acid or bromic acid; $2\text{HBrO}_3 + \text{I}_2 = 2\text{HIO}_3 + \text{Br}_2$.

It is a white, crystalline solid which is decomposed at 170° into water and its anhydride. Its stability is in keeping with its heat of formation, + 57.8 Cal. It forms stable salts with the basic oxides and the salts usually crystallize well. They may be prepared by treating the respective hydroxides with iodine just as they were treated with chlorine in forming the corresponding chlorates;



Potassium iodate, KIO_3 , is the most important salt of iodic acid.

164. Periodic Acid, HIO_4 , is analogous to perchloric acid both in its structure and its chemical character. It may be produced by treating perchloric acid with iodine;

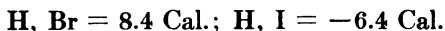


The free acid crystallizes well, decomposes when heated above 133° into water, oxygen, and iodic acid anhydride, and is therefore a good oxidizing agent. Its salts may be produced by heating cautiously the corresponding iodates; $2\text{KIO}_3 = \text{KIO}_4 + \text{KI} + \text{O}_2$. They are unimportant.

THE HALOGEN FAMILY

165. The physical and chemical properties of these four elements—fluorine, chlorine, bromine, and iodine—show a striking uniformity. Thus, the atomic weight, specific gravity, and boiling point increase from fluorine to iodine. This progression is also seen in the relative intensity of their coloring. Fluorine is yellow-green, chlorine is greenish-yellow, while bromine and iodine are respectively reddish-brown and black. This gradation in color-intensity is also to be observed in many of their compounds. Thus, silver fluoride and silver chloride are white, silver bromide is yellowish-white, and silver iodide possesses a pronounced yellow color. These attributes seem to bear some definite relation to the atomic weight of the participating halogen; that is, the increase in color is associated with increase in atomic weight.

This progression is to be observed to some extent in their chemical attributes. Thus, the affinity for hydrogen decreases progressively with the increasing atomic weight. Of the four hydrogen derivatives, HF, HCl, HBr, and HI, the hydrogen fluoride is much the most stable, while hydrogen iodide is the least so. This is in harmony with their respective heats of formation from the elements:



In their oxygen compounds the reverse order obtains. Fluorine does not combine with oxygen; the oxides of chlorine are very unstable, and decompose spontaneously or upon being gently heated; the pentoxide of iodine is a stable solid under ordinary conditions; while the oxides of bromine have not been isolated.

The same progressive stability is to be observed in the oxygen acids of these elements; further, these oxygen acids *increase in stability with increase in their oxygen content*: thus,

HClO , HBrO , and HClO_2 are feeble acids whose solutions decompose spontaneously, especially when exposed to direct sunlight; HClO_3 , HBrO_3 , and HIO_3 are stable in water solution even upon boiling; HClO_4 , HBrO_4 , and HIO_4 are more stable than their corresponding acids which contain *three* oxygen atoms. This progressive stability is to be observed also in the *salts* of these acids.

These and other facts have led to the grouping of these four elements into a "natural family." A general view of these relations may be had from the following table:

TABLE XVI

PHYSICAL PROPERTIES	FLUORINE	CHLORINE	BROMINE	IODINE
Atomic weight.....	19	35.45	79.96	126.85
Specific gravity.....	1.15 (liquid)..	1.15 (liquid)..	3.2 (liquid)	4.95 (solid)
Boiling Point.....	-187°	-40°	63°	184°
Color.....	pale green ..	greenish yellow.	brown ..	black
CHEMICAL PROPERTIES				
Formation of the hydrogen derivatives	Under all circumstances	In sunlight	In direct flame..	By indirect means
Affinity for oxygen.	None	Slight..	Unknown	Strong
COMPOUNDS WITH:				
Hydrogen.....	HF	HCl	HBr	HI
Heat of formation.	37 Cal.	22 Cal.	8.4 Cal. ..	-6.4 Cal.
Oxygen.....	None	Cl_2O ...	Unknown	I_2O_5
Oxygen and hydrogen	None	HClO HClO_2 HClO_3 HClO_4	HBrO HBrO_3 HBrO_4	 HIO_3 HIO_4

EXERCISES

1. Would fluorine act upon metallic sodium?
2. How would the resulting compound act when electrolyzed?
3. Why are glass bottles which are used to hold potassium fluoride always more or less opaque?

4. Why are the oxides of chlorine unstable?
5. What would be the properties of calcium hypochlorite, if the oxides of chlorine were strong exothermic compounds?
6. Why is additional heat unnecessary when bleaching with calcium hypochlorite?
7. Why is potassium chlorate more stable than potassium hypochlorite?
8. What would be the effect of mixing a large quantity of KClO_3 and H_2SO_4 ?
9. Why will chlorine replace iodine in potassium iodide? Would bromine show a like reaction? Why?
10. Would chlorine replace fluorine in hydrogen fluoride?

CHAPTER XII

THE OXYGEN GROUP OF ELEMENTS: GROUP II.

It was pointed out in the preceding chapter that the physical and chemical attributes of the halogens bear a definite relation to their atomic weights, and that the affinity for oxygen increases and the affinity for hydrogen decreases with atomic weight. It will be interesting to see whether four other elements whose atomic weights show a similar rate of increase bear the same relations toward their oxygen and hydrogen derivatives. Four such elements are Oxygen, Sulphur, Selenium, and Tellurium. The following table shows the likeness in the atomic weights of the two groups:

Elements	Oxygen	Fluorine	Sulphur	Chlorine
Atomic Wt.	16	19	32.06	35.45

Elements	Selenium	Bromine	Tellurium	Iodine
Atomic Wt.	79.2	79.96	127.6	126.85

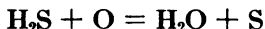
The hydrogen and oxygen derivatives of the second group of elements are very similar. Thus they each combine with two atoms of hydrogen, and the products, excepting water, are poisonous gases which have a strong odor. They combine with two atoms of oxygen and form compounds of the general type RO_2 . These oxides are acid anhydrides (excepting ozone, O_3).

SULPHUR, S (AT. WT. 32.06)

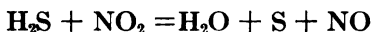
166. For the preparation and properties of sulphur, see page 122.

COMPOUNDS OF SULPHUR

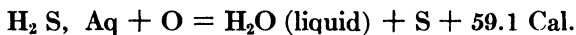
167. Hydrogen Derivatives.—Sulphur combines with hydrogen in different proportions, but the monosulphide, H_2S (hydrogen sulphide), is the most important. For its method of preparation and properties, see page 29. It is comparatively unstable, dissociating slowly at 400° into sulphur and hydrogen. When its solution in water is exposed to the air, it is decomposed and sulphur separates;



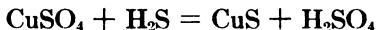
A similar decomposition always takes place when H_2S is exposed to the action of NO_2 , N_2O_3 , or N_2O_5 :



These reactions are in harmony with the heats of formation of the participating substances. Thus, in the first equation the heat relations are expressed by the graph,

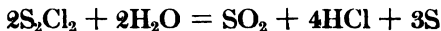


Hydrogen sulphide is a dibasic acid. Its two hydrogens are readily replaced by bases, forming the corresponding sulphides:



This property may be shown by passing H_2S gas through dilute solutions of salts of tin, copper, cadmium, antimony, etc.

168. Halogen Derivatives.—Sulphur forms compounds with the halogens in which the affinity (as measured by the stability of the compounds) decreases from fluorine to iodine. All of these derivatives are decomposed by water, yielding oxygen compounds of sulphur and a halogen acid. Thus,



This department shows that sulphur is essentially negative in its chemical relations except when associated with the more negative halogens. Sulphur monochloride, S_2Cl_2 , will serve to represent this type of derivatives. It is a yellowish liquid which boils at 139.2° . Its density is 67.5, which corresponds to the formula S_2Cl_2 .

169. Oxygen Derivatives.—Sulphur forms two important oxides:

SO_2 , sulphur dioxide

SO_3 , sulphur trioxide

I. *Sulphur Dioxide*, SO_2 (p. 132), possesses the character of a weak acid anhydride, since its solution in water forms sulphurous acid. It is a very strong exothermic compound; $S, O_2 = 71$ Cal. Consequently it is very stable, and is dissociated into its elements only at a high temperature.

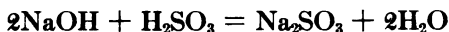
II. *Sulphur Trioxide*, SO_3 .—It was shown on page 133 that sulphur trioxide is formed when a mixture of sulphur dioxide and oxygen is passed over hot platinum-black. When the product is cooled to 10° in dry air, it crystallizes in long, transparent needles, or an asbestos-like mass. It is a strong exothermic compound, its heat of formation being 103.2 Cal. It fumes strongly in moist air and combines with water with great energy, forming sulphuric acid: $SO_3 + H_2O = H_2SO_4$.

This reaction is attended with the evolution of considerable heat; $SO_3, Aq = 39.1$ Cal.

170. Sulphurous Acid, H_2SO_3 , is not known in the free state because it breaks up readily into water and its anhydride, SO_2 . That it probably exists in dilute aqueous solution is suggested by two facts:

a. When the acid solution is neutralized by an alkaline hydroxide, a salt is formed in which the negative radical is

SO₃. The formation of such a salt may be expressed by the hypothetical graph,



b. The solution of sulphur dioxide in water liberates heat, which indicates chemical action; SO₂, Aq = 7.7 Cal. The comparatively small quantity of heat which is set free indicates that the acid is not very stable. Experiments show this to be the case.

Sulphurous acid contains two replaceable hydrogen atoms; it therefore forms two classes of salts—sulphites and hydrogen sulphites (bisulphites).

171. Salts of Sulphurous Acid.—*Sodium Sulphite*, Na₂SO₃, is a white crystalline solid which is the most important of the commercial sulphites. It is used extensively in photography* and to some extent as a preservative. When a small quantity of it is mixed with acid fruit juices, sulphur dioxide is set free. Sulphur dioxide dissolves in the liquid and retards or wholly prevents fermentation.

172. Sulphuric Acid, H₂SO₄.—This is one of the most important acids. It is used extensively in the manufacture of bleaching powder, soda, alum, and many fertilizers, in the refining of oils, chloroform, and other chemical compounds, in bleaching cotton goods, in dyeing, calico printing, etc. Its manufacture is a large industry. Plants for its preparation have been built in England, Germany, France, The United States, etc. The annual output is very great, England alone producing approximately 900,000 tons. There are two chief methods used in its preparation. One consists in oxidizing sulphur dioxide to sulphur trioxide by means of hot platinum and air, and dissolving the sulphur trioxide in water. Another

* Sodium thiosulphate (hyposulphite) is a different compound.

method, called the common or "English" method, consists in oxidizing sulphur dioxide in the presence of watery vapor, air, and an oxide of nitrogen.

173. Preparation of Sulphuric Acid.—Sulphur dioxide does not unite with the oxygen of the air without the aid of some other substance. In the English process, this substance is nitrogen peroxide, NO_2 . In the presence of sulphur dioxide NO_2 gives up one atom of oxygen to form SO_3 , and it, in turn, is reduced to NO . The nitric oxide therefore acts as a carrier of oxygen. Its action in oxidizing the sulphur dioxide to sulphur trioxide may be expressed by the graph, $\text{SO}_2 + \text{NO}_2 = \text{SO}_3 + \text{NO}$.

The reduced nitrogen oxide will combine with oxygen from the air, and form nitrogen peroxide; $2\text{NO} + \text{O}_2 = 2\text{NO}_2$.

The regenerated nitrogen peroxide NO_2 then acts upon an additional quantity of sulphur dioxide, and the above reaction is repeated.

I. Laboratory Method of Preparation.—The entire process is illustrated in the following experiment:

EXPERIMENT 61. *Perform this experiment under the hood.*—In Fig. 48, A is a wide-mouthed bottle with two openings, through one of

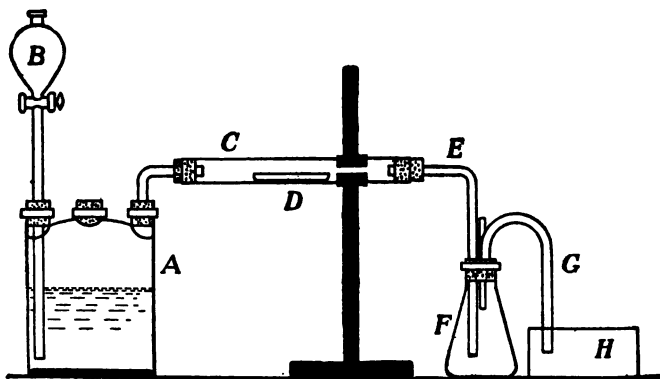
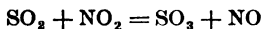


FIGURE 48

which is passed a separatory funnel B. The other has an exit tube which is connected with C. C is an ordinary glass tube about 20 cm. long and 1.5 cm. wide. F is a small Erlenmeyer flask which is connected with C by E and with H by G. D is a porcelain boat. H contains a strong solution of sodium hydroxide, which absorbs any gases that may escape from F.

Process.—Put about 200 cc. of a saturated solution of sodium bisulphite (or sodium sulphite) into A, fill the boat* D with concentrated nitric acid, connect the apparatus as shown in the cut, and heat the tube at D just hot enough to give off red fumes of NO_2 from the nitric acid in the boat. When the red fumes begin to come off, pass a slow stream of sulphur dioxide from A into the tube C and the flask F. This is readily done by adding concentrated sulphuric acid from B, drop by drop, to the solution of sodium bisulphite in A. The sulphur dioxide will be oxidized to sulphur trioxide by the nitrogen peroxide;



Let the action continue 5 to 10 min. If the apparatus is quite dry, crystals of sulphur trioxide will settle upon the walls of the tube C and the flask F. Stop the action, remove the boat, and spray the walls of C and F with water, to dissolve any sulphuric acid or sulphur trioxide which may adhere to them. Put the water into an evaporating dish, and concentrate it to a small volume. The presence of sulphuric acid in the residue may be shown by two simple reactions.

a. Moisten a strip of filter paper with some of the concentrated solution, and dry it at 100° . The formation of a black spot where the solution touched the paper shows the presence of sulphuric acid. This department finds an explanation in the fact that strong sulphuric acid possesses a powerful affinity for water. The molecule which gives to paper its characteristic attributes is composed of carbon, hydrogen, and oxygen. The last two elements are present in the proportion to form water and these are withdrawn, leaving the free carbon, which is black.

b. Dilute a small portion of the concentrated solution, and add a few drops of barium chloride solution. A white precipitate shows the presence of sulphuric acid.

II. *The Commercial Method of Preparation.*—The manufacturer of sulphuric acid utilizes the chemical reactions given in Experiment 61. It is usually carried on in large rooms lined with sheet lead. Two such rooms are shown in A, A', Fig. 49. J is an ordinary brick furnace, in which the sulphur in iron

* A piece of glass-wool or asbestos may be used.

pyrites (FeS_2) is oxidized to SO_2 . G is a tower, usually about 40 ft. high, which is filled with coarse pieces of fire-clay or other

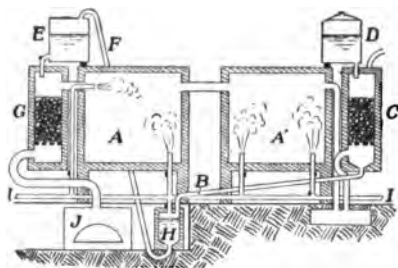


FIGURE 49

non-combustible material. E is a reservoir which is connected with the tower G and the pipe F, which is, in turn, in communication with the pump H. The tower C is similar to G, except that it is filled with coarsely powdered coke or pumice stone. The pipe

I I, is connected with a steam boiler not shown in the cut.

Process.—The sulphur in the pyrites is oxidized to sulphur dioxide in the furnace J, from which it passes, mixed with air, into the base of the tower G, thence up through the stone filling and into the first lead chamber. In some works the furnace is fitted with pots containing sodium nitrate and sulphuric acid. These give off the vapor of nitric acid, which passes up through the tower G along with the sulphur dioxide and air. There are other works where the nitric acid is introduced directly into the first and second lead chambers.

The mixture of nitric acid, air, and sulphur dioxide is exposed in the first chamber to hot steam from the pipe I. The simplest form of the reactions which take place may be represented by the graphs,

1. $2\text{HNO}_3 + \text{SO}_2 = \text{H}_2\text{SO}_4 + 2\text{NO}_2$
2. $2\text{NO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{NO}$
3. $2\text{NO} + \text{O}_2 = 2\text{NO}_2$
4. Reaction is repeated

Any *unoxidized sulphur dioxide* and *unreduced nitrogen peroxide* pass into the second chamber A', where they are again exposed to an atmosphere of hot steam and air, and the action again proceeds as in A. The sulphuric acid collects upon the floor of the chamber and is drawn off. If any of the oxides of nitrogen escape from A', they must pass up through the coke mixture in the tower C, which prevents their escape.

Pure concentrated sulphuric acid is allowed to flow slowly from the reservoir D, and percolate through the coke until it reaches the base of the tower. When the oxides of nitrogen which escape from

A' come in contact with this acid, they are absorbed by it, producing a crystalline compound.

The acid then flows through B into the pump H, by which it is lifted through F into the reservoir E. From this point it flows slowly through the filling in G to its base, where it is exposed to fresh quantities of sulphur dioxide from the furnace J. The oxides of nitrogen contained in the acid which comes from E materially promote the further oxidation of the SO_2 to SO_3 .

It will be seen that the tower C (Gay-Lussac's Tower) is merely a contrivance to prevent the loss of any oxides of nitrogen. Theoretically a small quantity of nitric acid should oxidize an indefinitely large quantity of sulphur dioxide. The nitrogen peroxide is reduced to nitric oxide; the gas so produced takes additional oxygen from the air within the chamber, whereby it is changed again to nitrogen peroxide, and is again ready to oxidize an additional quantity of sulphur dioxide. It would seem that this process of oxidation and reduction of the oxides of nitrogen would continue indefinitely, but such is not the case. It is found in practice that small quantities of nitric acid must be added from time to time. There are two chief sources of waste: (1) the towers do not suffice to prevent the complete escape of the gases; (2) some of the oxides combine chemically with the sulphuric acid in the chambers, producing the crystalline compound mentioned above, which settles upon the walls and is known technically as "lead-chamber crystals."

The crude "chamber acid" is a brownish, oily liquid which contains from 60 to 64 per cent of acid. It contains considerable water, from which it is in part separated by evaporation in leaden pans. When the acid reaches a concentration of from 75 to 77 per cent, it attacks the pans so energetically that its further concentration must be carried on in platinum or glass vessels. By this process an acid is obtained which has a specific gravity of about 1.84. Such an acid is pure enough for all ordinary commercial purposes, but to make it chemically pure it must be distilled. The hot acid possesses such powerful chemical activity that it is necessary to carry on the distillation in retorts of glass or platinum.

174. Properties of Sulphuric Acid.—In its purest and most concentrated form, sulphuric acid is a colorless, oily

liquid of about 1.85 specific gravity, which begins to vaporize at 338°. When it is heated to 400°, it dissociates into sulphuric acid anhydride and water; at a dull red heat the anhydride is further decomposed into SO₂ and O. Hence boiling sulphuric acid is a powerful oxidizing agent.

The affinity of the acid for water is so great that much heat is evolved when they are mixed. When sulphuric acid and water are mixed in approximately equivalent quantities, this relation may be expressed quantitatively by the graph,



In mixing the strong acid with water, the acid should be poured into the water, or the sudden evolution of much heat may produce steam and cause an explosion.

175. Salts of Sulphuric Acid.—This acid contains two replaceable hydrogen atoms. It therefore forms two classes of salts, the neutral sulphates, in which both of the hydrogen atoms of the acid have been replaced by a metal, and the bisulphates (also called acid sulphates), in which only one of the hydrogen atoms has been replaced.

There are many sulphates, such as those of copper, zinc, magnesium, iron, lead, and sodium, which are of commercial importance. These may be prepared by dissolving the corresponding metallic oxide or carbonate in sulphuric acid, and allowing the salt to crystallize.

SELENIUM, SE (AT. WT. 79.2)

176. In 1817 Berzelius discovered that the red deposit which is found in the lead chambers of most of the sulphuric acid manufactories is made of a finely divided metal which he called Selenium.

This element is found, usually associated with sulphur, in many and widely distributed minerals, chief among which are

Cuprous selenide, Cu_2Se ; Silver selenide, Ag_2Se ; and Eukairit, $\text{Cu}_2\text{Se} \cdot \text{Ag}_2\text{Se}$. It is also found in small quantity in iron pyrites. When iron pyrites is used as the raw material from which to obtain sulphur dioxide for the preparation of sulphuric acid, the selenium is oxidized to SeO_2 . This oxide is so easily condensed that it collects in the flue of the furnace used in roasting the pyrites, and this flue-dust is the richest material from which to extract the selenium.

177. Properties of Selenium.—The physical properties of selenium depend upon the method by which it is prepared, for it possesses several allotropic modifications. It usually comes into the trade in sticks which have a grayish color and metallic luster. It is very similar to sulphur in its chemical properties.

COMPOUNDS OF SELENIUM

178. Hydrogen Selenide, H_2Se , is a colorless, poisonous gas which dissolves rather freely in water, and forms a feebly acid liquid. This solution shows properties similar to a like solution of hydrogen sulphide. Hydrogen selenide is an endothermic compound, its heat of formation being -5.4 Cal. (Fabre).

179. Halogen Derivatives.—These compounds are analogous to the corresponding sulphur compounds, but they are more stable.

180. Oxygen Derivatives.—1. *Selenium Dioxide*, SeO_2 , is always formed when selenium is burned in the air or in an atmosphere of oxygen. At ordinary temperatures, it is a solid, but it volatilizes without decomposition at 320° . It dissolves readily in water, forming an acid liquid which, when evaporated slowly to dryness, yields large colorless prisms of selenious acid, H_2SeO_3 . It is therefore an acid anhydride.

Selenious acid is dibasic, forming selenites with bases, but these salts possess little commercial importance.

2. *Selenium Trioxide*, SeO_3 , has not been isolated. When, however, an aqueous solution of selenious acid is treated with chlorine gas, it is oxidized to selenic acid;



If the solution is concentrated until it reaches a specific gravity of about 2.62, an oily liquid which contains about 95 per cent of H_2SeO_4 (selenic acid) is obtained.

TELLURIUM, Te (At. Wt. 127.6)

181. This rare element, discovered by Müller in 1782, is less abundant than selenium. It is found both free and combined in certain gold ores, and is also found associated with bismuth, silver, lead, and some other metals. The pure substance is a silver white, brittle solid of 6.25 specific gravity, which melts at 452° . It is like sulphur in its chemical properties.

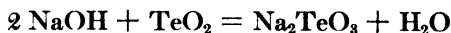
COMPOUNDS OF TELLURIUM

182. **Hydrogen Telluride**, H_2Te , may be prepared by heating zinc telluride, ZnTe , or iron telluride, FeTe , with dilute hydrochloric acid. It is a colorless gas, which dissolves sparingly in water, and forms a colorless liquid which has the properties of a like solution of hydrogen sulphide. It is an endothermic compound, its heat of formation being -19.4 Cal. (Fabre).

183. **Halogen Derivatives.**—These compounds are similar to the corresponding sulphur and selenium derivatives.

184. **Oxygen Derivatives.**—1. *Tellurium Dioxide*, TeO_2 , is formed when tellurium is burned in air or in oxygen.

It is a white, crystalline, sublimable solid, which is almost insoluble in water, but dissolves readily in a hot, concentrated solution of sodium hydroxide, forming sodium tellurite, Na_2TeO_3 :



Tellurium dioxide is therefore tellurous acid anhydride.

2. *Tellurium Trioxide*, TeO_3 , is formed when telluric acid, H_2TeO_4 , is heated to dull redness. It is not affected by water, dilute acids, or weak alkalis. Concentrated potassium hydroxide dissolves it, forming K_2TeO_4 . It is therefore telluric acid anhydride.

185. Tellurous Acid, H_2TeO_3 , may be prepared by dissolving the tellurium in concentrated nitric acid. It is dibasic, forming salts which are similar in their physical and chemical properties to the corresponding selenites.

186. Telluric Acid, H_2TeO_4 , forms colorless prisms which dissolve sparingly in water to a weak acid liquid. It is a dibasic acid, combining with bases to form salts, the tellurates, which possess little commercial importance.

THE OXYGEN FAMILY

187. The grouping together of oxygen, sulphur, selenium, and tellurium is based upon the uniformity in the structure of their most important derivatives. A certain relation prevails between the atomic weights and the physical attributes of the free elements. Thus the specific gravity, boiling point, and melting point increase as the atomic weight increases. Their affinity for the halogens increases with tolerable regularity as the atomic weight increases. OCl_2 is an exceedingly unstable, explosive gas under ordinary conditions. It even explodes when brought

into contact with sulphur, phosphorus, or other readily combustible material. Sulphur dichloride, SCl_2 , is a dark-red liquid which boils at 64° , and undergoes only partial decomposition at that temperature. The tetrachlorides of selenium and tellurium are white, crystalline compounds which may be vaporized without wholesale decomposition. The affinity of oxygen, sulphur, selenium, and tellurium for hydrogen seems to decrease with rise in atomic weight. This is to be observed in the temperature at which their respective hydrides dissociate:

H_2O , bright red heat

H_2Se , dull red heat

H_2S , red heat

H_2Te , dull red heat

The decreasing affinity for hydrogen with rise in atomic weight of the elements is also shown by the heats of formation of the respective hydrogen derivatives. Thus H_2O is a strong exothermic compound; H_2S is slightly exothermic; but H_2Se and H_2Te are both decidedly endothermic.

The following table contains data which make clear many of these relations:

TABLE XVII

PROPERTIES.	OXYGEN.	SULPHUR.	SELENIUM.	TELLURIUM.
Atomic Weight.....	16	32.06	79.2	127.6
Specific Gravity.....	.899 (at -130°)	2.05 (rhombic)	4.5 (crystalline)	6.25
Boiling Point.....	-186° (1 Atm.)	445° (volatile)	665° (volatile)	452° (volatile)
Hydrogen Compounds. * Heat of Formation....	H_2O $\text{H}_2, \text{O} = 57$	H_2S $\text{H}_2, \text{S} = 4.5$	H_2Se $\text{H}_2, \text{Se} = -5.4$	H_2Te $\text{H}_2, \text{Te} = -19.4$
Oxygen Compounds... Heat of Formation....	O, O_2 (gas) $\text{O}, \text{O}_2 = -32.4$	SO_2 (gas) $\text{S}, \text{O}_2 = 71$	Se O_2 (solid) $\text{Se}, \text{O}_2 = 57.7$	Te O_2 (solid) $\text{Te}, \text{O}_2 = 77$
Oxygen Acids.....		H_2SO_3 (?) H_2SO_4 (liquid)	$\text{H}_2\text{Se O}_3$ (solid) H_2SeO_4 (liquid)	H_2TeO_3 (solid) H_2TeO_4 (solid)

* Data from Thomsen.

188. Comparison of Halogen and Oxygen Families.

—The study of the elements of the halogen and oxygen groups shows three very suggestive facts: (1) in the case of both groups the affinity for hydrogen decreases with rise in the atomic weight. Thus, hydrogen fluoride is very stable, while hydrogen iodide decomposes in diffused light or on being boiled. Hydrogen oxide is so stable that it may be heated to near $1,000^{\circ}$ without dissociating, while hydrogen telluride is readily decomposed under ordinary conditions. (2) The opposite relation obtains with the oxygen derivatives. The affinity increases rather uniformly with increase in the atomic weight. Thus, fluorine forms no oxide, while the pentoxide of iodine is stable below 300° . The dioxide of oxygen (ozone) decomposes spontaneously, while the dioxide of tellurium is so stable that it may be sublimed without decomposition. (3) The hydrogen derivatives of the halogens are all *acids*, whose strength decreases with rise in atomic weight. The hydrogen derivatives of the oxygen group are also acids (excepting water, which is neutral) whose strength also decreases with increasing atomic weight. Some insight into the *degree* of these variations may be had from the following table, if the heat of formation be taken as a measure of stability:

E	At. Wt.	Der.	H. of F.	React.	E	At. Wt.	Der.	H. of F.	React.	A=acid N=neutral
F	19	HF	37	A	Cl	35.5	HCl	22	A	
O	16	H ₂ O	57	N	S	32.06	H ₂ S	4.5	A	

E	At. Wt.	Der.	H. of F.	React.	E	At. Wt.	Der.	H. of F.	React.	A=acid N=neutral
Br	79.06	HBr	8.4	A	I	126.8	HI	-6.4	A	
Se	79.2	H ₂ Se	-5.4	A	Te	127.6	H ₂ Te	-19.4	A	

It is of importance to note that the acidity of these derivatives, as they are here arranged, decreases from left to right, and from top to bottom.

EXERCISES

1. Why does sulphur always separate, when hydrogen sulphide is exposed to the action of free oxygen?
2. Would Cl, Br, or I decompose hydrogen sulphide? Why?
3. Why is sulphurous acid, H_2SO_3 , unstable?
4. At what temperature will strong sulphuric acid become an oxidizing agent?
5. Why is it so difficult to expel all water from strong sulphuric acid?
6. Would free oxygen decompose hydrogen selenide?
7. Why is ozone more active chemically than atmospheric oxygen? Is it more active than pure oxygen?
8. Would sulphur dioxide decompose ozone?
9. Could ozone be prepared by heating pure oxygen to a high temperature? Why?
10. Would ozone decompose hydriodic acid?
11. Could hydrogen sulphide be prepared from iron sulphide and nitric acid? Why?
12. Give two reasons for the belief that sulphur is fundamentally negative in its electrical properties.

CHAPTER XIII

THE NITROGEN GROUP OF ELEMENTS: GROUP III.

It is now proposed to select four or five other elements whose atomic weights may be arranged in a series like the one above (p. 217), and to ascertain what relation, obtains between them and the elements of the preceding groups. Such a series is found in the nitrogen group of elements, which includes nitrogen, phosphorus, arsenic, antimony, and bismuth. These five elements are grouped together partly because of their atomic weight relations to the members of the preceding groups, but also because of the similarity in the attributes of their halogen, hydrogen, and oxygen derivatives. (1) They each (excepting bismuth) combine with three atoms of hydrogen to form gaseous products which are irritating or poisonous. (2) They combine with three atoms of halogen and form derivatives which are generally unstable, especially in the presence of water. (3) Their chief oxygen compounds are of two types: R_2O_3 and R_2O_5 . These oxides show a gradation in properties from very strong acid anhydrides to weak bases.

NITROGEN, N (At. Wt. 14.04)

189. For its preparation and properties, see page 64; for the preparation and properties of ammonia, see page 68.

COMPOUNDS OF NITROGEN

190. Hydrogen Derivatives.—Ammonia is an important compound of hydrogen and nitrogen. Although it is a gas under ordinary conditions, it may be liquefied by cooling and by subjecting to pressure. This liquid is a refrigerating agent. Any liquid must absorb heat in changing into a gas, and if the

absorption is rapid, heat will be withdrawn rapidly from the surrounding medium, and its temperature will be correspondingly lowered. Liquid ammonia evaporates with great rapidity, and hence is used in the preparation of artificial ice.

191. The Manufacture of Artificial Ice.—There are two types of ice machine which use ammonia as the refrigerating

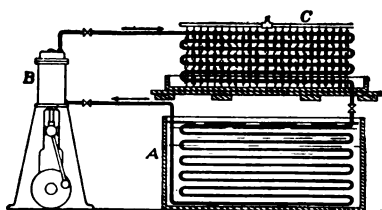


FIGURE 50

agent, the *Absorption* and the *Compression* machine. In the compression type, the freezing is produced by the alternate condensation and expansion of anhydrous ammonia in iron pipes. There are three fundamental steps in the process,

viz., compression, condensation, and expansion of the ammonia gas. These operations may be traced in the action of the machine which is shown in Fig. 50.

I. Compression.—The gaseous ammonia is compressed in the pump B by a pressure which varies from 125 to 175 pounds per square inch. During the compression, considerable mechanical force of the pump is transformed into sensible heat, and the compressed gas becomes heated.

II. Condensation.—It is driven from the compressor pump B into the condenser C. The condenser consists of a series of pipes or coils which are cooled by a spray of cold water. The compression of the ammonia in the pump B, and its subsequent cooling in the condenser C, liquefies it.

III. Expansion.—The liquid is collected in a strong tank, from which it passes through a very fine opening, called an expansion valve, into a series of iron pipes which are imbedded in the brine tank or congealer A. The arrangement of the tank B for receiving the liquid ammonia, with its expansion valve C, may be seen in Fig. 51.

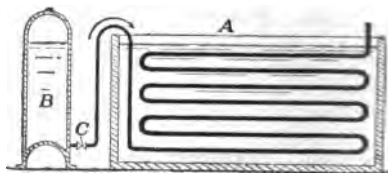
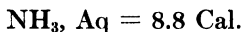


FIGURE 51

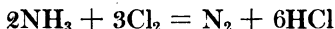
The liquid ammonia, upon expanding into gas, absorbs heat. This heat is withdrawn from the brine in which the pipes or coils A are placed, and causes its temperature to fall below the freezing point of fresh water. The gaseous ammonia then returns to the compressor pump B, (Fig. 50) and the process is repeated.

The water which is to be converted into ice is run into large iron moulds, usually 8x15x35 in., and these are lowered to at least four-fifths of their depth into the cold brine. They are thus surrounded by a freezing mixture, and the water in them solidifies in about twelve hours.

192. Chemical Properties of Ammonia.—It was pointed out on page 68 that ammonia dissolves in water, forming an alkaline solution. Ammonium hydroxide is probably formed. It has never been isolated, because it breaks up spontaneously into ammonia and water. This may be readily understood from its rather low heat of formation:



It was pointed out in Experiment 32 (p. 71) that chlorine withdraws the hydrogen from the ammonia molecule according to the equation,



This reaction is also accounted for by the heat of formation:



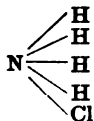
The reader will recall that so much heat was set free in tube E, Fig. 23, that it was necessary to cool it with a stream of cold water. The above equation explains this phenomenon.

Ammonia unites *directly* with acids to form the corresponding salts:

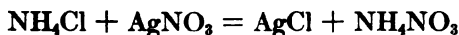


This direct union is due to the power of nitrogen to increase its valence to 5.

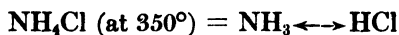
The structure of ammonium chloride, NH_4Cl , may be represented by the graph,



Although, because of its instability, the group NH_4 has never been isolated, there are reasons to believe that it acts as a unit, or radical. One is its power to replace positive ions in the formation of salts, as illustrated by the following:



193. Salts of Ammonia.—Ammonia combines with acids, forming salts which are more stable than its hydroxide, but even the salts are decomposed by heat into NH_3 and the acid:



If the decomposition products are volatile, they pass off into the surrounding air, where, upon cooling, they recombine to form the original salt. This property may be shown by the following experiment:

EXPERIMENT 62. Put 2 gm. of dry ammonium chloride into a dry test-tube and heat the salt very strongly in the bunsen flame. A heavy white deposit, called a sublimate, will be formed in the cold part of the tube.

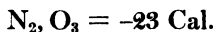
194. The Halogen Derivatives of Nitrogen.—These compounds are so very unstable that they are readily decomposed by heat or direct sunlight (see page 180).

195. Oxygen Derivatives of Nitrogen.—There are five well-known oxides of nitrogen: N_2O , NO , N_2O_3 , NO_2 or N_2O_4 ,

and N_2O_5 . The affinity of nitrogen for oxygen is so slight that its oxides cannot be formed readily by direct union of the elements. When a mixture of the two elements is drawn over hot platinum-black, they unite to some extent, but ordinarily their union must be brought about by some *indirect* means. The oxides are usually prepared by decomposing nitric acid or some nitrate.

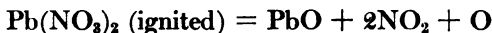
I. *Nitrogen Monoxide*, N_2O .—For the method of preparation and general attributes of this gas, see page 146.

II. *Nitrogen Trioxide*, N_2O_3 .—For the method of preparation and properties of this compound, see page 147. When it is cooled to -20° , it becomes a liquid which boils at a temperature above $+4^\circ$ and decomposes into NO , and NO_2 . Nitrogen trioxide does not exist, therefore, at ordinary temperatures except in aqueous solution. Its instability is in harmony with its heat of formation,



It probably forms nitrous acid when it dissolves in water.

III. *Nitrogen Peroxide*, NO_2 , or N_2O_4 .—This compound is easily prepared by heating lead nitrate:



If the gases are passed through a tube surrounded by a freezing mixture, the oxygen escapes, but the nitrogen peroxide is condensed to a colorless liquid which begins to boil at 22° . The density of the vapor points to the formula, N_2O_4 . Above 140° it is decomposed completely into two molecules of NO_2 . Nitrogen peroxide is dark brown in color.

When the vapor of NO_2 is conducted into ice-water, nitrous and nitric acids are formed:



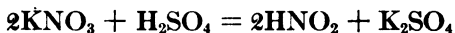
Nitrogen peroxide is therefore a mixed acid anhydride.

IV. *Nitrogen Pentoxide*, N_2O_5 , does not exist free in nature. It may be prepared by distilling a mixture of phosphorus pent-

oxide and nitric acid. It forms colorless crystals which are so unstable that they explode violently when heated quickly. They dissolve in water with the evolution of considerable heat and form nitric acid:



196. Nitrous Acid, HNO_2 , has not been isolated. When its salts are acidified, brown vapors are at once formed, which are a mixture of NO_2 and NO . A type of these changes may probably be expressed by the graphs,



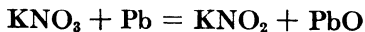
The spontaneous decomposition of the free nitrous acid explains the fact that it is both an oxidizing and a reducing agent. NO_2 gives up its oxygen very readily, and is therefore a strong oxidizing agent, while NO absorbs oxygen and is therefore a reducing agent.

The oxidizing properties of nitrous acid are brought out in the next experiment.

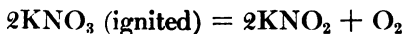
EXPERIMENT '63. Saturate 20 cc. of water with hydrogen sulphide. To a small portion of the liquid, add a solution of copper sulphate. A black precipitate, CuS , results (Test for H_2S). Acidify a solution of potassium nitrite, which contains about one-tenth gram of the salt, with dilute sulphuric acid, and mix with the hydrogen sulphide solution; the mixture will become milky from the separation of free sulphur. Again test the solution with copper sulphate. Does the hydrogen sulphide still exist?

197. Salts of Nitrous Acid.—The hypothetical formula, HNO_2 , suggests that nitrous acid is monobasic. Its salts, the nitrites, are prepared in three ways:

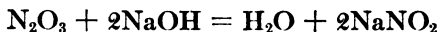
1. By fusing an alkali nitrate with an oxidizable metal:



2. By igniting potassium nitrate:



3. By conducting N_2O_3 or its decomposition products into the solution of a basic oxide or hydroxide:



The nitrites are mostly yellow and stable compounds which dissolve readily in water. They are found in small quantities in rain and flowing water, in some plants, and in the soil.

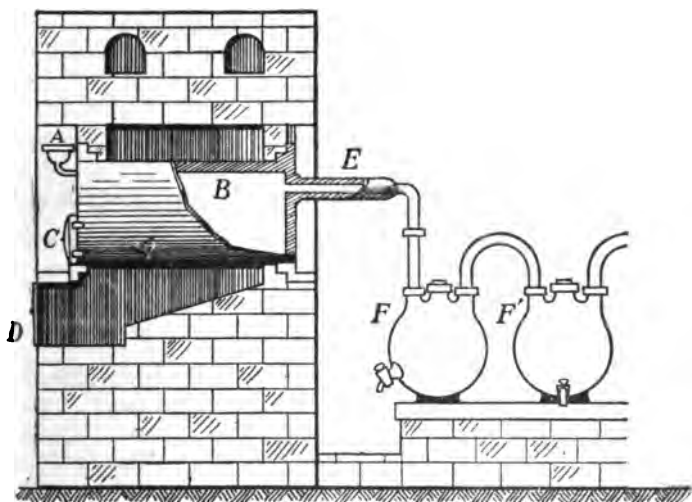


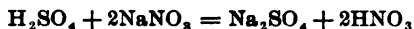
FIGURE 52

198. Nitric Acid.—For preparation of this acid in the laboratory, and for its physical properties, see page 147.

Nitric acid is manufactured on a large scale by distilling a mixture of sodium nitrate and sulphuric acid.

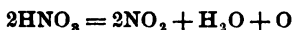
Process.—A charge of sodium nitrate is put into the large cast-iron cylinder B, Fig. 52, the door C is made gas-tight, a sufficient quantity of commercial sulphuric acid is run in through the funnel A,

and the mixture is gently heated by the fire in D. The chemical changes may be expressed by the graph,



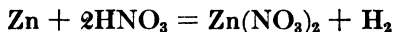
The nitric acid distills over and is collected in the large earthenware receivers F F'. The last of the receivers is usually connected with a tower filled with coke, over which water is sprayed to absorb any vapors which may escape from the receivers.

Commercial nitric acid contains approximately 68 per cent by weight of the pure acid. The most concentrated quality, which contains about 99.8 per cent of acid, is a thick, colorless fluid which has a specific gravity of about 1.54. Boiling decomposes strong nitric acid into water, an oxide of nitrogen, and oxygen:

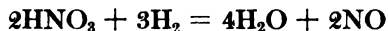


Hence strong nitric acid is a powerful *oxidizing agent*, and, conversely, it is easily reduced. Its oxidizing power is greatly increased when it contains nitrogen peroxide. "Fuming nitric acid" is very concentrated and contains sufficient free nitrogen peroxide, NO_2 , to give to it a deep red color.

199. The Action of Nitric Acid on Metals.—The reaction between nitric acid and the metals seems anomalous. Thus, when sulphuric or hydrochloric acid acts upon zinc, the corresponding salt is formed and hydrogen is set free; but when a fairly concentrated solution of nitric acid (10 per cent) acts upon zinc, the nitrate is formed but no hydrogen is set free. The normal course of the reaction would be,



Such reaction probably occurs, but the nascent hydrogen (see p. 82) reduces part or all of the excess of nitric acid to water and an oxide of nitrogen. The exact reaction depends largely upon the temperature and concentration of the acid. Probably the most common reaction may be represented by the graph,



It follows that when nitric acid of the usual concentration (1:10) acts upon a metallic element, a colorless gas, NO , is

given off which absorbs oxygen on exposure to the air and forms red-brown fumes, NO_2 .

200. Salts of Nitric Acid.—A nitrate may be made by dissolving a metal, its oxide, hydroxide, carbonate, or some other easily decomposable salt in nitric acid and crystallizing the product. The nitrates are generally soluble in water. They are unstable and are readily decomposed by heat. There are three chief types of this decomposition:



Since either oxygen or an oxide of nitrogen (which is an oxidizing agent) is always given off, all nitrates are powerful oxidizing agents when they are heated to the point of decomposition. This property is illustrated in the following experiment.

EXPERIMENT 64. Place three gm. of potassium nitrate in a small crucible supported on a triangle, heat it until the contents fuse, and then very cautiously add a small piece of charcoal, paper, cloth, or wood. The oxidation will be speedy and complete.

EXPERIMENT 65. The speed of oxidation may be increased as follows: Thoroughly pulverize and intimately mix one gm. of potassium nitrate and 0.2 gm. of charcoal; heat an iron crucible (or a piece of sheet iron) to redness, and, keeping the face well away from it, throw a small portion of the mixture upon the hot surface. The oxidation of the charcoal will proceed with such speed as to be practically instantaneous, and therefore explosive.

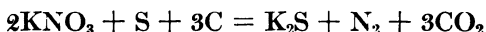
Speedy oxidation is of fundamental importance in all explosives that are of practical value. This is illustrated in the properties of gunpowder.

201. Black Gunpowder was invented and used as an explosive as early as 1350 A. D. It is a mixture of

sulphur, charcoal, and potassium nitrate. A good powder is made of

	PER CENT
Sulphur.....	10
Carbon	15
Potassium nitrate.....	75
	100

To insure the maximum speed of oxidation, the ingredients are reduced to an impalpable powder, mixed intimately, and pressed into a compact mass, which is dried and ground. Upon ignition there is a great and sudden evolution of gas, which causes the explosion. One gram of powder yields approximately 300 times its own volume of gas. The expansive power is very greatly increased by the high temperature, which is said to approximate 2,000°. This energy is derived largely from the latent heat of the NO₃ radical, which is a strong endothermic compound. The actual course of the chemical reaction is complicated. It is usually represented in its simplest form by the graph,



The mechanical equivalent of a pound of powder, i.e., its power to do work, is equivalent to lifting 486 tons through one foot.

Smokeless gunpowder will be discussed elsewhere.

PHOSPHORUS, P (AT. WT. 31)

202. Preparation and Uses of Phosphorus.—For the preparation and properties of phosphorus and its allotropic modifications, see pages 129-131.

The chief use of phosphorus is in the manufacture of matches. It ignites spontaneously when heated to 50°, and it serves therefore to start combustion. The head of a match is made up of phosphorus, an oxidizing compound, and an

adhesive—usually glue. Sometimes other neutral substances are added to give it bulk. One such mixture is made of

	PER CENT
Phosphorus.....	17
• Glue	21
Sodium nitrate.....	38
Red lead.....	24

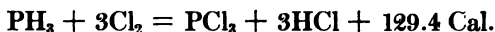
When the head is rubbed against a rough surface the friction produces heat, which raises the temperature at the point of friction to 50° or above. The phosphorus ignites. Oxygen is set free from the oxidizing agent, which so intensifies the combustion that the whole mass bursts into flame. Safety matches contain no phosphorus, but are made of antimony sulphide and glue, together with an oxidizing agent, e.g., potassium chlorate. This mixture does not ignite when rubbed against an ordinary surface. It requires contact with a special surface, usually made of red phosphorus, sand, antimony sulphide, and glue.

COMPOUNDS OF PHOSPHORUS

203. Hydrogen Derivatives.—The most important hydrogen compound of phosphorus is hydrogen phosphide, PH_3 , also called phosphine. It is a colorless, poisonous, very inflammable gas, which is insoluble in water, and possesses a penetrating garlic-like odor. The simplest method for its preparation is to heat a mixture of yellow phosphorus and concentrated sodium hydroxide in the absence of air, and collect the escaping gas over water free from dissolved oxygen.

204. Chemical Properties of Phosphine.—Phosphine resembles ammonia in its chemical action, but it is much less basic. Its solution in water gives only a feeble alkaline reaction.

When mixed with chlorine it explodes with violence, and the evolution of heat;

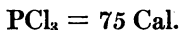
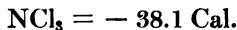


It combines with hydrochloric acid at a low temperature to form a salt, phosphonium chloride, which is similar in its structure to ammonium chloride:



PH_4 , termed phosphonium, acts as a radical. The formation of phosphorus trichloride, as above, shows that phosphorus possesses a greater affinity for chlorine than does nitrogen.

205. Halogen Derivatives.—Phosphorus forms two classes of halogen compounds, PR_3 and PR_5 , in which R stands for a halogen atom. Phosphorus trichloride has a sharp, penetrating odor, and fumes strongly in moist air. Its vapor density is 68.6, corresponding to the formula, PCl_3 . The unequal stabilities of nitrogen trichloride and phosphorus trichloride are in harmony with their heat relations. Nitrogen trichloride is a very strong endothermic compound, while phosphorus trichloride is strongly exothermic;



206. Oxygen Derivatives of Phosphorus.—There are two well-known oxides of this element, the trioxide and the pentoxide.

I. *The Trioxide*, P_2O_3 , is formed when phosphorus is burned in an insufficient quantity of air. It is a white, amorphous solid, whose vapor possesses a strong garlic-like odor. It melts at 22.5° and boils at 173° in an atmosphere of nitrogen

or carbon dioxide. It dissolves easily in water, forming phosphorus acid;



P_2O_3 is therefore phosphorus acid anhydride.

II. *Phosphorus Pentoxide*, P_2O_5 , is formed when phosphorus is burned in oxygen or an excess of air. It is a white, flocculent mass, which dissolves in *cold* water with great energy, forming metaphosphoric acid, HPO_3 ;



207. Phosphorus Acid, H_3PO_3 , may be prepared by dissolving P_2O_3 or PCl_3 in water. It is a dibasic acid, since it contains but two replaceable hydrogen atoms, and forms salts of the general types, MH_2PO_3 and M_2HPO_3 .

208. The Phosphoric Acids.—There are three types of acids which belong to this group:

Orthophosphoric acid,* H_3PO_4

Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$

Metaphosphoric acid, HPO_3

209. Orthophosphoric Acid.—This acid may be regarded as the substance from which the pyro- and metaphosphoric acids are derived. Thus, when one molecule of phosphoric acid gives up one molecule of water, metaphosphoric acid is formed.



When *two* molecules of phosphoric acid give up *one* molecule of water, pyrophosphoric acid is formed;



Of these acids, orthophosphoric is far the most important. It may be prepared by dissolving phosphorus pentoxide in *hot*

* Also called phosphoric acid.

water or by oxidizing phosphorus with strong nitric acid. When the aqueous solution is evaporated to dryness, the acid is obtained in colorless hard crystals. It is tribasic and forms three types of salts, e.g.:

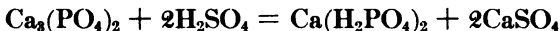
Sodium di-hydrogen phosphate, NaH_2PO_4

Sodium mono-hydrogen phosphate, Na_2HPO_4

Sodium phosphate, Na_3PO_4

Salts of the first type are called primary phosphates; salts of the second and third types, secondary and tertiary phosphates.

210. Salts of Phosphoric Acid.—The tertiary phosphates of most metals are insoluble in water;* the primary phosphates are usually soluble. Tertiary calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is a white salt which is present in bone-ash, and in uncalcined bones. Bone-meal, which is a modified form of bone-ash, owes its value as a fertilizer largely to the presence of this salt. As it will not dissolve in water, it cannot be absorbed by the roots of plants. In order that it may become more available, the tertiary phosphate must be changed to the primary phosphate. This is usually done where the fertilizer is prepared, by digesting the tertiary phosphate with sufficient commercial sulphuric acid to transform it into the primary phosphate;

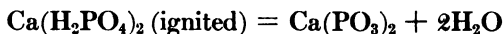


A mixture of primary calcium phosphate and some nitrogenous materials is known commercially as "Superphosphates." Primary calcium phosphate is also used extensively in the preparation of certain varieties of baking powder.

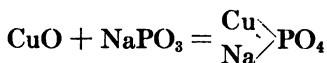
211. Metaphosphoric Acid and its Salts.—When any primary phosphate is strongly ignited, it loses two molecules of

*Sodium and potassium phosphates are soluble.

water and is transformed into the corresponding metaphosphate;



When sodium or potassium phosphate is ignited, a glass-like compound, e.g., NaPO_3 , is obtained, which dissolves oxides of certain metals, forming brilliantly colored compounds. This is because the negative radical PO_3 tends to absorb oxygen and become PO_4 ;



This action is shown in Experiment 66.

EXPERIMENT 66. Bend the end of a platinum wire into a closed loop, heat it to redness, plunge it into some dry primary sodium phosphate, NaH_2PO_4 or sodium ammonium hydrogen phosphate, $\text{NaNH}_4\text{HPO}_4$, and heat it very strongly in the outer zone of the blow-pipe (p. 112) until the contents of the loop cease to bubble. If sodium ammonium hydrogen phosphate is used, heating will effect the following changes;

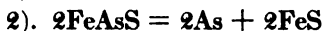
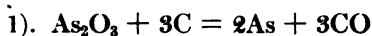


Touch the hot bead to some powdered copper oxide and again expose it to a strong heat from the outer zone of the blow-pipe. A beautiful blue-green bead will be formed. These beads of the metaphosphates are used in analytical chemistry to detect the presence of certain oxides.

ARSENIC, As (At. Wt. 75)

212. At least three compounds of arsenic were known to the ancients. As early as the eighth century Gerber prepared arsenic oxide, but the element was not isolated until about the thirteenth century. Later Schröder (1694), and Brandt (1738) prepared the metal in a pure form. It is found very sparingly in the uncombined state, but its compounds are abundant and widely distributed. Chief among them are realgar, As_2S_2 ; orpiment (auripigment), As_2S_3 ; arsenical pyrites, FeAsS ; and arsenic oxide, As_2O_3 . Arsenic is prepared (1) by reducing

the ore with charcoal, or (2) by roasting the ore in ovens, and condensing the product upon a cold surface;



213. Properties of Arsenic.—The crystalline variety of arsenic is a steel-gray, brittle solid of 5.73 specific gravity, which ignites at 180° , and burns with a blue flame, forming arsenic trioxide. Like phosphorus, this element forms allotropic modifications. Thus, at 860° its vapor density is 150, which gives a molecular weight of 300 and a molecule of four atoms, As_4 ; at a very high heat the density falls to 75, which gives a molecule of two atoms, As_2 . It combines with some elements directly, forming products which are all poisonous both to plants and animals. It resembles phosphorus in its fundamental chemical properties.

COMPOUNDS OF ARSENIC

214. Hydrogen Derivatives.—Arsenic forms two compounds with hydrogen, of which hydrogen arsenide, or arsine, AsH_3 , is the most important. This compound may be prepared by reducing the soluble compounds of arsenic with nascent hydrogen. It is a colorless, ill-smelling gas, insoluble in water and acid. It burns readily in the air, forming water and arsenious oxide. It is a fearful poison when inhaled, and for this reason the very greatest precaution is necessary in working with it. It may be prepared and detected by the method of Marsh:

EXPERIMENT 67. *Caution! Perform this experiment under the hood. On no account inhale the gas.*

A 300 cc. flask, A, Fig. 53, is provided with a separatory funnel E, and connected with a tube of hard glass C (which is drawn out to a point D) by the curved tube B, which contains fused calcium chloride for drying the gas. Introduce 20 gm. of granulated zinc

into A, connect the apparatus as shown in the cut, run in from E sufficient dilute sulphuric acid (1:8) to cover the zinc, and heat the flask until a brisk evolution of hydrogen ensues. After ten minutes of brisk effervescence, to insure the removal of all air, ignite the gas at D and then allow two or three cc. of a dilute solution of sodium arsenite (1:50), or any other soluble salt of arsenic, to flow into the flask. Do not add too much of the arsenical solution, or the evolution of the gas will become so vigorous as to be annoying, and perhaps dangerous. Keep the gas burning at D. In a short

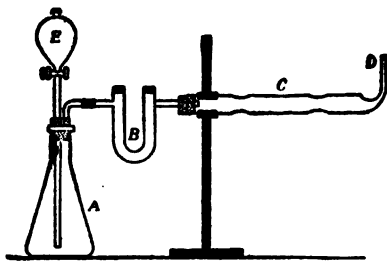


FIGURE 53

time the gas flame will take on a peculiar blue-violet color, attended with the escape of white fumes and a garlic-like odor. When a cold porcelain dish is held in the flame, the hydrogen of the arsine continues to burn, but the arsenic, which is less combustible, settles upon the dish in the free condition, forming a blue-black mirror of great brilliancy. This "arsenical mirror" is made of thin layers of arsenic, and is soluble in a solution of bleaching powder (page 194).

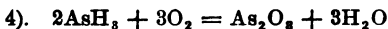
The chief chemical changes may be expressed by the graphs,

- 1). $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2 \uparrow$
- 2). $\text{As}_2\text{O}_3 + 3\text{H}_2 = 2\text{As} + 3\text{H}_2\text{O}$

The nascent arsenic and hydrogen then unite to form the arsenetted hydrogen:



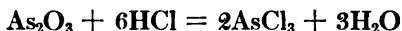
The complete combustion of the gas forms As_2O_3 and H_2O



Arsine differs from hydrogen phosphide in that it does not combine with hydrochloric or hydrobromic acid. It forms no compounds analogous to the ammonium and phosphonium salts.

215. Halogen Derivatives of Arsenic.—These are analogous to the corresponding compounds of phosphorus and nitrogen. The trichloride may be prepared by passing dry

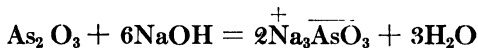
chlorine over pulverized arsenic, or by heating arsenious oxide, As_2O_3 , with strong hydrochloric acid, and collecting the distillate in a cooled receiver;



It is a colorless liquid which boils at 134° . Its vapor density is 90.5, which corresponds to the formula, AsCl_3 . It is decomposed by water into arsenious oxide and hydrochloric acid. Its relative stability is explained by its heat of formation, 71.4 Cal., which shows it to be a strong exothermic compound.

216. Oxygen Derivatives of Arsenic.—This element forms two oxides, As_2O_3 and As_2O_5 .

I. *Arsenic Trioxide* is a common by-product in the metallurgy of other elements. Its vapor is conducted into long, cylindrical stacks, or cooling rooms, in which it is condensed and settles upon the walls in thick white layers. It is removed and purified by subliming it in iron vessels. It is found in the trade as a glass-like substance or an amorphous powder. It dissolves sparingly in water, forming a colorless, sweetish liquid, which is extremely poisonous. It is also readily soluble in the hydroxides of the alkali metals;

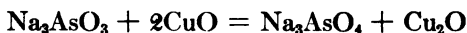


This shows that it is an acid anhydride.

II. *Arsenic Pentoxide* may be obtained by heating arsenic acid, H_3AsO_4 , to redness. It is a glassy compound which breaks up on further heating into As_2O_3 and O_2 . It dissolves gradually in water, forming arsenic acid; $\text{As}_2\text{O}_5 + 3\text{H}_2\text{O} = 2\text{H}_3\text{AsO}_4$. It is therefore arsenic acid anhydride.

217. Arsenious Acid, H_3AsO_3 , does not exist free. It is probably formed when arsenious oxide dissolves in water, but it is decomposed when the solution is evaporated to dryness. It is

a tribasic acid which forms salts of the type, M_3AsO_3 . These salts have a tendency to form compounds with four atoms of oxygen in the negative radical, M_3AsO_4 . They are in consequence strong reducing agents;



218. Arsenic Acid, H_3AsO_4 , crystallizes in rhombic prisms or needles. It may be prepared by dissolving metallic arsenic or arsenious acid anhydride in strong nitric acid, evaporating the resulting solution to a syrup, and allowing the mass to crystallize at a low temperature. It is a tribasic acid which forms primary, secondary, and tertiary arsenates, analogous in structure to the corresponding phosphates.

ANTIMONY, SB (AT. WT. 120.2)

219. Preparation and Properties of Antimony.—

This element, which was first isolated by Valentinus in the fifteenth century, is found widely distributed in nature, chiefly as stibnite, Sb_2S_3 . It is prepared by fusing 100 parts of stibnite, 42 parts of crude iron, 10 parts of sodium sulphate, and 3 parts of charcoal; $Sb_2S_3 + 3Fe = 2Sb + 3FeS$. It is a silver-white, brittle metal which melts at 432° . It is permanent in the air at the ordinary temperature, but burns readily when heated above its melting point. It is insoluble in dilute hydrochloric, or sulphuric acid, but hot concentrated nitric acid changes it to an oxide. Like arsenic and phosphorus, it combines directly with nascent hydrogen, and forms antimonetted hydrogen, also called hydrogen antimonide, or stibine.

COMPOUNDS OF ANTIMONY

Antimony forms two types of derivatives, the antimonious and the antimonic.

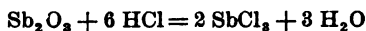
220. Hydrogen Derivatives.—The most important hydrogen compound of antimony is antimonetted hydrogen, SbH_3 , or stibine. It may be prepared by the same process as that outlined for arsine (Experiment 67). It is a colorless gas, comparatively insoluble in water and acids, and burns with a green flame which gives off white fumes of antimony oxide. It is decomposed at red heat into antimony and hydrogen. When a cold surface is put upon its flame, it leaves a mirror of metallic antimony (Experiment 67), which differs from the arsenical mirror in that it is insoluble in a solution of bleaching powder or sodium hypochlorite. Stibine does not combine with the halogen acids to form salts.

221. Halogen Derivatives.—Antimony shows a greater affinity for the halogens than do the preceding elements of this group. The trichloride, SbCl_3 , may be prepared by sprinkling finely powdered antimony into dry chlorine gas. The action will proceed with such vigor that flashes of yellow flame will be seen. A yellowish residue of antimony chloride will be formed. When chemically pure, SbCl_3 is a colorless solid which melts at 73° and boils at 223° . Its vapor density is 113.3, corresponding to the formula, SbCl_3 . It dissolves in dilute hydrochloric acid, forming a colorless liquid. Much water decomposes it and precipitates an insoluble white powder, SbOCl . This shows that antimony is a weak "metalloid," i.e., its basic properties are so slight that it cannot hold a strong negative like chlorine. The *relative* stability of its chloride in water shows, however, that it is *more* basic in character than arsenic, phosphorus, or nitrogen.

222. Oxygen Derivatives.—Three oxides of antimony have been studied:—the trioxide, Sb_2O_3 ; the tetroxide, Sb_2O_4 ; and the pentoxide, Sb_2O_5 .

1. *The trioxide* is formed by oxidizing antimony in the air, or with hot nitric acid. It is a white crystalline powder, insoluble in water,

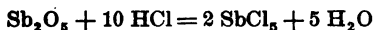
but soluble readily in strong hydrochloric acid, forming antimony trichloride;



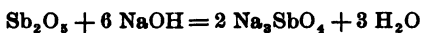
It is here a basic oxide. It also dissolves readily in the caustic alkalis, forming salts of the general type MSbO_3 , in which it acts as an acid anhydride.

When a metal has the power to act both as a negative and a positive radical, according to conditions, it is called a *metalloid*.

2. *Antimony Pentoxide*, formed by heating antimonious acid, H_3SbO_4 , is a yellow amorphous mass which dissolves in strong hydrochloric acid, forming antimony pentachloride;



It is readily soluble in the caustic alkalis, forming the corresponding salts of antimonious acid;



It acts, therefore, both as a basic oxide and as an acid anhydride.

3. *Antimonious acid*, H_3SbO_4 , is formed when *aqua regia* acts upon metallic antimony. It separates as a bulky, gelatinous precipitate. It behaves like orthophosphoric acid when heated. At 100° it gives up one molecule of water and forms pyroantimonious acid, $\text{H}_4\text{Sb}_2\text{O}_7$; at 200° it gives off another molecule of water and forms metantimonious, HSbO_3 . These acids are analogous to the corresponding acids of phosphorus.

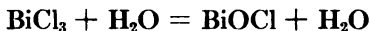
BISMUTH, BI (AT. WT. 208.5)

223. Preparation and Properties of Bismuth.—This element is found free in veins in granite or slate. Its sulphide, Bi_2S_3 , is also used as an ore. The ore is first roasted; this changes any arsenic which may be present into volatile arsenic trioxide, which escapes. The resulting mass consists of a mixture of metallic bismuth, its trioxide, unaltered bismuth sulphide, and other impurities. It is then mixed with carbon and iron, and fused. The carbon withdraws any oxygen, and the iron combines with the sulphur. The bismuth, thus set free, filters to the bottom of the mass and is then drawn off. The last traces of arsenic are removed by fusing the powdered metal with saltpeter. It is a grayish-white, brittle metal, with a

peculiar reddish luster. It is permanent in the air at ordinary temperatures, but when heated to redness burns with a bluish flame, forming Bi_2O_3 . It differs from the preceding elements of this group in that *it does not form a hydrogen derivative*.

COMPOUNDS OF BISMUTH

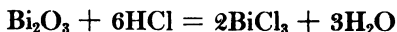
224. Halogen Derivatives.—Bismuth forms compounds with the halogens which have the general structure, BiR_3 , in which $\text{R} = \text{F}, \text{Cl}, \text{Br}$, or I . The chloride will illustrate these derivatives. It may be prepared by dissolving bismuth in *aqua regia* (3 vol. HCl : 1 vol. HNO_3) evaporating, and distilling the residue. It forms a white, fusible mass which melts at 227° and distills at about 435° . It dissolves in water, but the solution quickly clouds, owing to the loss of the chlorine and the substitution of oxygen;



This shows that bismuth possesses *some* of the attributes of a metalloid.

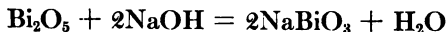
225. Oxygen Derivatives.—There are three known oxides of bismuth: Bi_2O_2 , Bi_2O_3 , and Bi_2O_5 .

1. *Bismuth Trioxide*, Bi_2O_3 , is a yellow powder which may be formed by heating the nitrate. It is insoluble in water and strong alkalis, but dissolves readily in strong acids to form the corresponding salts of bismuth;



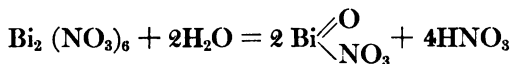
It does not seem to possess any acid anhydride properties.

2. *Bismuth Pentoxide*, Bi_2O_5 , possesses *very weak* anhydride properties. It is said to form salts with the alkali metals, in which it appears as a negative radical;



226. Salts of Bismuth.—The failure of its oxides to show pronounced anhydride properties places bismuth clearly in the

line of the *true bases*, and its deportment toward the mineral acids with which it forms normal salts also sustains this view. The nitrate, $\text{Bi}_2(\text{NO}_3)_6$; sulphate, $\text{Bi}_2(\text{SO}_4)_3$; chloride, BiCl_3 ; etc., are well known. Of these salts the nitrate is perhaps the most important. It is decomposed by much water into a basic salt which is known in medicine as "subnitrate of bismuth";



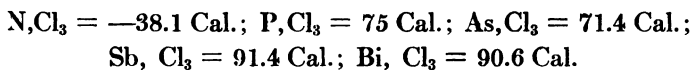
It is a white powder which is used as a remedy in stomachic and intestinal disorders, and as a cosmetic.

THE NITROGEN FAMILY

227.—The members of this group form hydrogen, halogen, and oxygen derivatives which are structurally similar. Their chemical properties show a gradual change from nitrogen to bismuth. Thus, the affinity for a given element seems to increase or decrease with atomic weight. The hydrogen derivatives have the general structure RH_3 , and the affinity of these elements for hydrogen *decreases* from nitrogen to bismuth. This may be noted in the temperature at which the hydrogen compounds dissociate, and in their heats of formation:

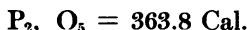
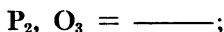
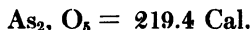
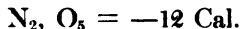
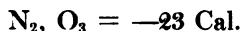
	N, H_3	P, H_3	As, H_3	Sb, H_3	Bi
Temp. of Dissociation			Red heat	Red heat	
Heat of Formation... ..	11.8 Cal.	11.6 Cal.	-11.7 Cal.	-84.5 Cal.	

The reverse order obtains in the halogen derivatives. Thus, bismuth trichloride is the most stable, and nitrogen trichloride is the least so:



In general the affinity of the elements of this group for oxygen increases from nitrogen to bismuth. Thus, the affinity of

phosphorus for oxygen is greater than that of nitrogen. The oxides of nitrogen are strong endothermic compounds, while the corresponding oxides of phosphorus are as strongly exothermic. This relation, as well as the general trend of the affinity for oxygen, may be seen in the following thermal values.*



The following table gives a general view of the attributes of some derivatives of this group, and their relations to the atomic weights of the elements from which they are derived.

TABLE XVIII

	NITROGEN	PHOS- PHORUS	ARSENIC	ANTIMONY	BISMUTH
Atomic Weight.....	14.04	31	75	120.2	208.5
Specific Gravity.....	0.885 (liquid)	1.83 (octa- hedral)	5.73 (cryst.)	6.7	9.7
Trichloride	NCl_3	PCl_3	AsCl_3	SbCl_3	BiCl_3
1. H. of F.†.....	-38.1	75	71.4	91.4	90.6
2. Boiling Point.....		78°	134°	223°	435°
Oxygen Derivatives.. and their	N_2O_3 N_2O_5	P_2O_3 P_2O_5	As_2O_3 As_2O_5	Sb_2O_3 Sb_2O_5	Bi_2O_3 Bi_2O_5
Chemical properties..	Anhydrides	Anhydrides	Anhy- drides	Weak an- hydrides; also basic	Decidedly basic
Principal Acids.....*	HNO_2 HNO_3	H_3PO_3 H_3PO_4	H_3AsO_3 H_3AsO_4	HSbO_2 H_3SbO_4	Does not form acids
Hydrogen Derivatives and their properties.....	NH_3 Strong base	PH_3 Weak base..	AsH_3 Neutral....	SbH_3 Neutral!	

* Data from Dammer. † H. of F. = Heat of Formation.

EXERCISES

1. Would ammonia be a refrigerating agent, if it were a liquid under ordinary conditions?
2. Why is fuel necessary in making ice?
3. In making ice could liquid air be substituted for ammonia gas?
4. Will the oxides of nitrogen liberate iodine from hydriodic acid? Why?
5. Could sand be substituted for sulphur or carbon in gunpowder without materially influencing the qualities of the powder? Why?
6. What is superphosphate?
7. Would ground bones be good dressing for a lawn?
8. Would the sulphide of arsenic or of bismuth dissolve the more readily in strong hydrochloric acid?
9. Would the quality of gunpowder be improved if arsenic trioxide were substituted for potassium nitrate? Why?

CHAPTER XIV

THE CARBON GROUP OF ELEMENTS: GROUP IV.

The descriptive matter of the preceding chapter developed the reasons for arranging the elements to which it relates in a "natural family." The chemical significance of this arrangement is emphasized when the group is placed in juxtaposition with the oxygen and halogen families. The mutual relations of the elements of the three groups, and their hydrogen derivatives, are brought out in the following table:

TABLE XIX

	Element	At. Wt.	Derivative	Heat of Formation	Reaction.	Element	At. Wt.	Derivative	Heat of Formation	Reaction.
I. Halogen Group.....	F	19	HF	Cal. 37	A*	Cl	35.45	HCl	Cal. 22	A
II. Oxygen Group.....	O	16	H ₂ O	57	N†	S	32.06	H ₂ S	4.5	W.A.‡
III. Nitrogen Group.....	N	14.04	H ₃ N	11.8	Alk.‡	P	31	H ₃ P	11.6	W.‡ Alk.

	Element	At. Wt.	Derivative	Heat of Formation	Reaction	Element	At. Wt.	Derivative	Heat of Formation	Reaction	Element	At. Wt.	Derivative	Heat of Formation	Reaction
I..	Br	79.96	HBr	8.4	A	I	126.8	HI	-6.4	A					
II..	Se	79.2	H ₂ Se	-5.4	W.A.	Te	127.6	H ₂ Te	-19.4	W.A.					
III..	As	75	H ₃ As	-11.7	N	Sb	120.2	H ₃ Sb	-84.5	N	Bi	208.5			

It is to be noted in this arrangement of the elements that the affinity for hydrogen in each series *decreases* from left to right, and

* A = acid; † N = neutral; ‡ Alk. = alkaline; | W. A. = weak acid; § W. Alk. = weak alkali.

the acid properties decrease from the top downward. Thus, in the first three derivatives (HF , H_2O , NH_3), we have respectively an acid, a neutral, and a basic compound. In the hydrogen derivatives of chlorine, sulphur, and phosphorus the same relation prevails. In the next two series the same general order may be seen, although arsine and stibine are neutral and not basic in their properties. It will be observed that there are no elements corresponding to bismuth in the halogen and oxygen families. Such elements may exist, but they have not yet been discovered.

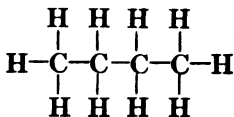
The properties of the hydrogen compounds as they are arranged in Table XIX show another important tendency, i.e., the *acid properties decrease* rather uniformly from left to right and the *basic properties increase* from top to bottom.

It becomes a matter of importance to discover whether or not this tendency to form basic compounds with increase in atomic weight of the participating element, is shown by four other elements whose atomic weights approximate, respectively, those of the preceding groups. Such a group of elements is found in carbon, silicon, tin, and lead. The elements of this group show certain similarities in their fundamental chemical properties, but they are not so patent as in the preceding groups. Indeed they may with advantage be divided into two sub-groups: A, Carbon and Silicon; and B, Tin and Lead.

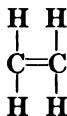
SUB-GROUP A

228. Carbon and Silicon.—These two elements are similar in their chemical and some of their physical properties. The normal valence is four, the halogen derivatives are much alike, their oxides are weak acid anhydrides, which form stable salts with basic hydroxides, while the acids which are made from them are unstable, decomposing readily into water and the acid anhydride. The fundamental difference in the chemical activity of the two elements is found in the extraordinary ability of carbon atoms to combine with each other to form carbon

chains. Thus four carbon atoms may combine in the following manner:



Or two or more atoms may be combined with four valences;



At times two atoms are held by six bonds; $\text{H}-\text{C}\equiv\text{C}-\text{H}$. As a result of this power of carbon to satisfy its own bonds, and thus form chains of carbon atoms, the number of possible carbon compounds is so great that their investigation constitutes a special phase of chemical science, known as "organic chemistry," because it was formerly believed that carbon compounds could be built up only through the life-activity of some plant or animal. Silicon does not possess the power of forming chains of atoms; consequently the number of its compounds is much less than that of carbon. A few compounds of the two elements will be studied to develop clearly their similarities.

CARBON, C (AT. WT. 12)

229. For the preparation and properties of carbon, see pages 31-32. Carbon is inactive at ordinary temperatures. It must be heated to a high temperature before it will combine with atmospheric oxygen, although the compound which results from such a combination is very strongly exothermic: $\text{C}, \text{O}_2 = 97 \text{ Cal.}$ The combustion usually continues with great energy, when the critical temperature is reached. Hence hot carbon will withdraw oxygen from many oxides. This was illustrated in the

action of the blow-pipe and charcoal on certain oxides (page 112), and the action of the blast furnace in reducing oxides of iron to the metallic condition (page 113). Advantage is taken of the particularly high temperature of combustion of graphite in the use of stove polish. It oxidizes, "burns off," only slowly, because the critical temperature at which graphite combines with oxygen is seldom reached or long maintained. Carbon also combines with basic elements at a very high temperature, e.g., $3,000^{\circ}$, to form a series of compounds called carbides, the most interesting of which is calcium carbide, CaC_2 .

COMPOUNDS OF CARBON

230. Calcium Carbide.—This substance is formed by heating a mixture of lime and coke in an electric furnace (Fig. 54.*). The mixture is put into the central cup and a powerful electric current is passed between the heavy carbon rods. This generates an intense heat, which effects the chemical changes in the mixture. The most important of these may be expressed by the graph,

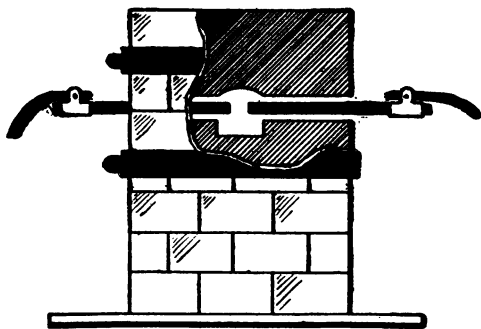
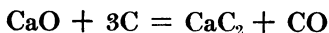


FIGURE 54



Commercial calcium carbide is a reddish, crystalline solid, stable in dry air, but decomposed by moisture into gaseous acetylene, C_2H_2 , and calcium oxide, CaO .

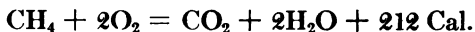
*There are different types of electric furnaces, but in all of them the heat is generated by an electric current passing between two carbon electrodes.

231. Hydrogen Derivatives.—The number of hydrogen derivatives of carbon (called hydrocarbons) is exceedingly large. Only a limited number of the most important can be described here. Chief among them is carbon tetrahydride, or methane, CH_4 . Methane gas may be obtained in a relatively pure state in the following manner:

EXPERIMENT 68. Put 10 gm. each of dry sodium acetate, and potassium hydroxide, or calcium hydroxide into a 200 cc. retort, connected with a cylinder for collecting the gas, and heat the mixture;



A colorless, odorless gas is collected, whose combustion in oxygen liberates a great deal of heat;



The flame possesses very little illuminating power. "Natural gas" (which is made up largely of methane) is a good fuel, but a poor illuminant. This is due to the fact that practically all of the carbon is burned to carbon dioxide (page 113).

232. Methane and Other Fuels.—Methane is formed during the natural decay of organic compounds, especially in swamps and beneath the surface where there is buried organic matter. The gas often collects in coal mines, and when mixed with air forms an explosive mixture called "fire-damp." It was pointed out in chapter X that the chlorophyll of the plant builds complex carbon compounds from the carbon dioxide and moisture which surround it. These complex molecules are made up of carbon, hydrogen, and oxygen. When such material is heated it is decomposed. Much of the hydrogen and oxygen and some of the carbon escape, but much of the carbon remains. The purity of the carbon will depend upon the completeness of these changes. During the great coal-forming periods of the earth's history, immense quantities of vegetable matter were accumulated in marshes. It was then covered by sediments,

and subjected to pressure. The changes in the composition of the vegetable material were slow, and the varying degrees of completeness with which the hydrogen was expelled (as, e.g., CH_4) are represented by the several types of fuel now in use.

1. *Peat* is vegetable matter which has lost only a small percentage of its hydrogen and oxygen. In most peat the structure of the woody fiber is distinct.

2. *Lignite*, a later stage, is a brown-black coal which possesses a more or less woody structure.

3. *Bituminous* or soft coal represents greater change. It contains much of the original hydrogen, some oxygen, and much of the carbon. When such coal is ignited, gaseous compounds of carbon and hydrogen, e.g., CH_4 , are set free, and their combustion gives a bright flame. If the coal is heated sufficiently without access of air, the gases may be collected, stored, and used for fuel. This is the basis for the preparation of artificial gas.

4. *Anthracite*, or hard coal, has had most of the hydrogen and oxygen expelled. When ignited, it gives off little gas, and therefore gives little flame. The blue flame over hard coal fires is due chiefly to the combustion of carbon monoxide. Anthracite coal cannot therefore be used for preparing artificial gas.

5. *Charcoal*, which is composed of carbon and a little mineral matter, is a final stage in the transformation of wood to inorganic carbon. It is a manufactured, not a natural fuel.

TABLE XX*

MATERIAL	CARBON PER CENT	HYDROGEN PER CENT
Wood	50.00	6.00
Peat	60.00	5.90
Lignite	70.00	5.00
Bituminous	88.00	5.60
Anthracite	94.00	3.40
Charcoal	96.00	0.60

* Data from Young. The figures in this table express the *average* proportions of carbon and hydrogen. It is not to be understood that the percentage of carbon or hydrogen in any sort of coal is a fixed quantity.

The general type of these changes is illustrated in Experiment 69.

233. Preparation of Illuminating Gas.—I. Laboratory Method.—The principal products formed by the destructive distillation of soft coal may be obtained by the process outlined in Experiment 69.

EXPERIMENT 69. A, (Fig. 55), is a 200 cc. retort of hard glass, and B a receiver for collecting the distillate. It is con-

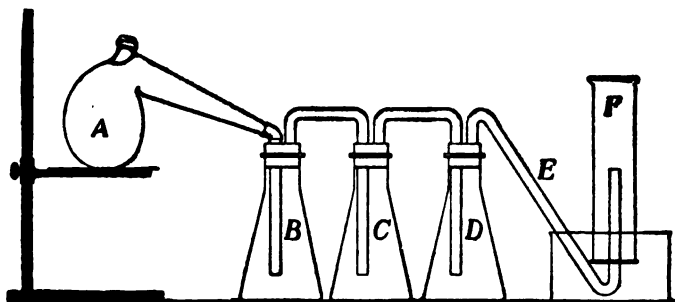


FIGURE 55

nected with the flasks C and D, which contain, respectively, water and a dilute solution of copper sulphate; F is a 400 cc. cylinder for receiving the gaseous products.

Put 30 gm. of finely powdered soft coal into the retort, connect the apparatus as shown in the cut, heat the retort until a steady flow of gas streams through the flasks, and then connect the tube E with the cylinder F, and continue the heat until F is filled with gas, and until a dark liquid has collected in B. The following products should be obtained:

1. The residue in A is a hard variety of carbon.
2. The liquid in B is a tarry substance.
3. The contents of C are strongly alkaline, and have a strong odor of ammonia.
4. Filter off the black precipitate in D, place it in a test-

tube, add from 2 to 3 cc. of strong hydrochloric acid, heat gently and note the odor of hydrogen sulphide.

5. The gas in F should burn with a white light.

II. *Manufacturer's Method.*—The commercial preparation of illuminating gas is based on the principles outlined in the laboratory method, but the apparatus which is used is outlined

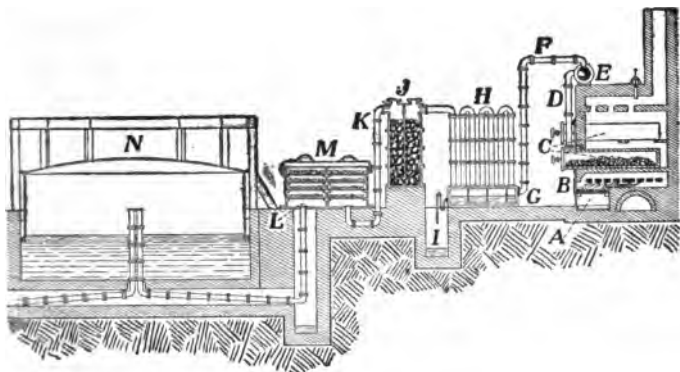


FIGURE 56

in Fig. 56. The process may be conveniently divided into five fundamental steps: (a) generating, (b) condensing, (c) scrubbing, (d) purifying, and (e) storing the gas.

(a) *Generating the Gas.*—Soft coal is thrown into the retorts C, which are of fire-clay, arranged in tiers of two or more, so that a single fire beneath the lowest will heat all above it. Such a group of retorts is called a bench.

The doors of the retorts are secured by heavy iron levers, so as to make them gas-tight. They are then heated to from 800° to $1,200^{\circ}$ for about four hours. All volatile products are thus expelled from the coal, and there remain in the retort two varieties of carbon: (1) a coarse and porous variety, which is *gas-coke*; and (2) a more or less crystalline variety, which adheres closely and firmly to the walls of the retort, the *gas-carbon*, from which electric light rods are manufactured.

The volatile products pass from the retorts through the main D, and the water-valve E, into the hydraulic main F, and thence into the condenser H. The main, D, is bent at right angles as shown in the cut, and dips into a vessel of water E. The gas passes through the water and into the hydraulic main. The water in E serves two purposes: (a) it withdraws much of the tarry substances from the gas, and (b) it prevents the gas from passing back into the retorts. The hydraulic main, F, serves to conduct the gas into the condenser, H, and to dissolve much of the remaining tar and ammonia.

(b) *Condensing the Gas.*—The hot gas, from which much of the tar, ammonia, and hydrogen sulphide have been removed,

passes into the condenser. This is an arrangement of pipes so fixed that the gas must circulate vertically through them. Here the gas is cooled, and most of the tar and ammonia are separated and drained off into the tar cistern, I.

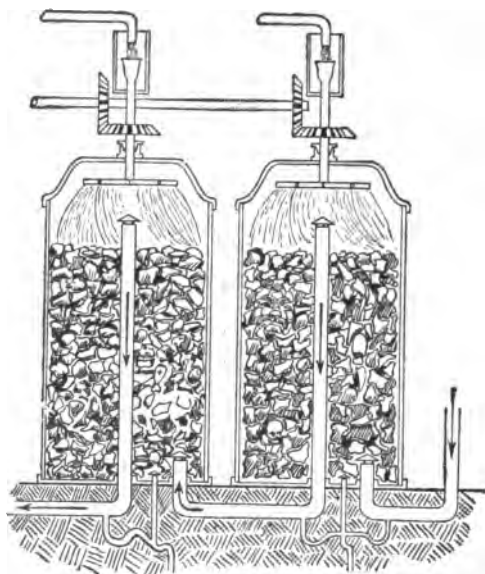


FIGURE 57

(c) *Scrubbing the Gas.*—The cooled and partly purified gas is drawn by an exhaustor into the

scrubber J. The chief feature of the scrubber is that water is constantly sprayed into the towers J, and runs slowly to the bottom. In some plants the gas comes in at the base of the

towers (Fig. 57), and rising through this spray, is washed very thoroughly. By this process, practically all of the remaining tar, and most of the hydrogen sulphide and ammonia are removed. The gas then passes from the top of the second tower into the purifier M.

(d) *Purifying the Gas.*—The purifiers, M, are shallow, rectangular iron boxes filled with slaked lime. Their interior construction is such that the gas which passes through them is exposed to a large surface of the lime, which fixes the carbon dioxide, and any remaining hydrogen sulphide;



(e) *Storing the Gas.*—The purified gas passes into the gas holder N, from which it is delivered to the distributing mains.

234. Illuminating Gas by Dissociation of Steam.—

The preparation of illuminating gas from steam is based upon two familiar facts:

(1) Steam is dissociated at about $1,000^\circ$ into hydrogen and oxygen; and (2) oxygen will form carbon monoxide when it acts upon an excess of incandescent carbon.

Such gas consists chiefly of H and CO. These gases produce flames which have a very low illuminating power. Hence the manufacturer must charge these products with higher hydrocarbons, such as ethane, propane, acetylene, etc., to give illuminating power. There are two chief steps in the manufacture of "water gas": (1) The dissociation of the steam and the formation of carbon monoxide, and (2) the charging of the gas with the higher hydrocarbons, called carburetting the gas.

(1) *Dissociating the Steam.*—This is effected by the apparatus shown in Fig. 58. The generator B is charged with anthracite coal, fired, and a strong blast of air is blown into it for about five minutes. The intense combustion thus produced not only raises the unburned coal to incandescence, but also heats the fire-clay in the carbureter

C, to a high temperature. The air is then shut off, the chimney is closed, and a blast of steam is forced up through the incandescent coal from the steam pipe A. Three fundamental reactions take place in the generator:

1. $\text{H}_2\text{O (dissociated)} = \text{H}_2 \longleftrightarrow \text{O}$
2. $\text{C} + \text{O}_2 = \text{CO}_2$
3. $\text{CO}_2 + \text{C} = 2\text{CO}$

(2) *Carburetted the Gas.*—The mixture of hydrogen and carbon monoxide passes to the top of the carbureter C, where it is mixed with a spray of petroleum oil from the pipe D. As the oil passes over the

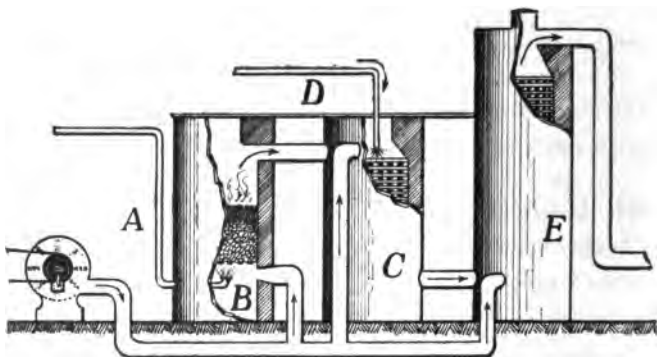


FIGURE 58

intensely heated fire-clay in the carbureter, it is dissociated into hydrocarbons, which are gases under ordinary conditions, and therefore will not liquefy when cooled. This dissociation of the oil is further promoted by passing the gases through the superheater, E.

The product is then scrubbed, purified, and stored as in the case of coal gas; or it is mixed with coal gas in order to increase its illuminating power, and then distributed to the consumer. The gas prepared by this process is commonly called "water gas."

235. Composition of Coal and Water Gas.—The composition of the two gases is given in the following table. It should be borne in mind that other samples of gas would probably give slightly different results.

TABLE XXI

CONSTITUENTS	WATER GAS PER CENT	COAL GAS PER CENT
Methane, CH_4	20.3	35.4
Hydrogen	32.0	48.7
Ethane, C_2H_6 , etc. ...	14.8	5.4
Carbon Monoxide....	27.2	6.5
Carbon Dioxide.....	3.0	1.3
Nitrogen.....	2.7	2.7

236. Properties of Illuminating Gas.—The foregoing analyses show that both coal and water gas are mechanical mixtures.

Water gas contains a larger percentage of carbon monoxide than coal gas and is therefore more poisonous.

The quantity of gas which a ton of coal will yield depends largely upon the quality of the coal, as will be seen from the following analyses.

TABLE XXII

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Cu. ft. of gas per ton of coal....	11,492	11,336	9,500	15,000	7,166	6,500	10,467

A ton of coal also yields, as by-products, about 1,200 pounds of coke, 125 pounds of tar, a small quantity of gas carbon, and several gallons of ammoniacal liquor.

237. Coal Tar.—Tar is used to some extent as a lubricant, for the preparation of tarred paper for building purposes, and as a paint for preserving woods. It is separated by fractional distillation into its most important constituents, some of which

have considerable commercial importance. These products are:

1. Benzene, etc.
2. Water which is charged with ammonia.
3. Heavy oils which contain creosote, carbolic acid, etc.
4. The pasty residue which remains in the retort is run into cooling pans, where it hardens to a brittle mass called asphalt.

Asphalt is used extensively in making coarse varnishes, and as a paint with which to protect timber from the injurious effects of water.

The watery liquids which are obtained from the condenser, II (Fig. 56), are the chief source from which the commercial supply of ammonia is obtained.

238. Halogen Derivatives of Carbon.—The halogens do not unite directly with carbon. The halogen derivatives are usually prepared by substituting chlorine or bromine for hydrogen in some hydrocarbon. The following series of chlorine derivatives have been prepared from methane:

1. $\text{CH}_4 + \text{Cl}_2 = \text{HCl} + \text{CH}_3\text{Cl}$, monochlormethane
2. $\text{CH}_4 + 2\text{Cl}_2 = 2\text{HCl} + \text{CH}_2\text{Cl}_2$, dichlormethane
3. $\text{CH}_4 + 3\text{Cl}_2 = 3\text{HCl} + \text{CHCl}_3$, trichlormethane
4. $\text{CH}_4 + 4\text{Cl}_2 = 4\text{HCl} + \text{CCl}_4$, tetrachlormethane

A statement concerning the last two derivatives will suffice.

1. *Trichlormethane*, CHCl_3 , is chloroform. It is a colorless, heavy liquid with an ethereal odor and a sweetish taste. It is usually prepared by treating common alcohol, $\text{C}_2\text{H}_5\text{OH}$, with bleaching powder.

2. *Tetrachlormethane*, CCl_4 , is a colorless liquid with an ethereal odor, which may be distilled without decomposition. Its stability is explained by its heat of formation, $\text{CCl}_4 = 21 \text{ Cal}$. All of these derivatives are stable in the presence of water.

239. Oxygen Derivatives of Carbon.—There are two known oxides of carbon;

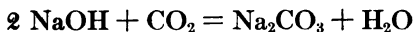
CO, carbon monoxide

CO₂, carbon dioxide

I. Carbon Monoxide.—In the discussion of steel manufacturing, it was pointed out that this gas possesses strong reducing properties. It is not an anhydride. It is a strong poison to all warm-blooded animals. Charcoal and hard coal fires give off considerable quantities of carbon monoxide. Open fires in which these materials are used are therefore dangerous.

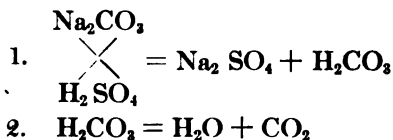
II. Carbon Dioxide.—It was pointed out on page 30 that this compound is a colorless, odorless gas which dissolves sparingly in water, forming an acid liquid which possesses the power to neutralize alkalis. It is therefore an acid anhydride. It is essentially different from carbon monoxide in its physiological effects. When the inspired air contains about 5 per cent of the dioxide, it prevents the exhalation of CO₂ from the tissues. They are thus deprived of the requisite amount of oxygen, and life cannot exist without it.

240. Carbonic Acid, H₂CO₃, is supposed to be formed when its anhydride, CO₂, is dissolved in water. It has never been isolated, because it breaks up readily into H₂O and CO₂. On boiling the liquid, the anhydride is completely expelled. The acid, or its anhydride, combines with bases to form stable salts, the carbonates; hence carbon dioxide is readily soluble in sodium hydroxide. This reaction, which is representative of a type, may be expressed by the graph,



Carbonic acid is a dibasic acid, and as such is capable of forming two classes of salts, the normal carbonates, e.g., Na₂CO₃, in

which *all* of the positive hydrogen has been replaced by a metal; and the acid carbonates (also called bicarbonates), in which only *one* of the hydrogen atoms has been replaced, e. g., NaHCO_3 , sodium bicarbonate. When *any* carbonate is acidified with a strong acid, the carbonic acid is set free, and decomposes at once into water and its anhydride;



The free carbon dioxide is so sparingly soluble in water that any appreciable quantity of it will escape in bubbles from the liquid. The liquid is then said to effervesce.

241. Effervescing Waters.—Carbonic acid is used in the preparation of effervescing waters, the chief representative of which is ordinary “soda water.”

The “fountain,” which is a stout-walled brass cylinder lined with zinc, is filled with water, then cooled to a comparatively low temperature, and the carbon dioxide is driven into it under two or three atmospheres pressure. The low temperature and the high pressure cause the water to absorb much more of the gas than it could were the temperature and pressure normal. Thus, water at 14° temperature and under *one* atmosphere of pressure will absorb its own volume of the gas; but at the same temperature and *three* atmospheres pressure, it will absorb approximately three times its volume of the gas. When such water is drawn off into an open glass, the diminished pressure allows about *two-thirds* of the gas to escape in bubbles. It is called “soda water,” presumably from the fact that the carbon dioxide was formerly made from soda and sulphuric acid.

Liquids which sparkle owe this property to the presence of dissolved carbon dioxide. Most running waters contain more or less of it in solution, and it gives to them a lively and refreshing flavor. Upon standing, the carbon dioxide and other gases escape, after which the water is said to taste “flat” or stale.

242. The Leavening Process.—Advantage is taken of the physical properties and the comparatively indifferent chemical character of carbon dioxide in the aeration, or leavening, of the dough from which bread, cakes, rolls, etc., are made. There are two fundamental types of the process,

1. Aeration through fermentation.
2. Aeration by chemical preparations.

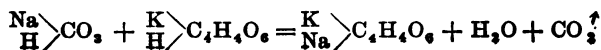
I. *Fermentation.*—When moist glucose, $C_6H_{12}O_6$, a substance strongly resembling ordinary sugar in its composition and properties, is acted upon by the yeast plant, it is decomposed into alcohol and carbon dioxide;



The constituents of the dough are acted upon by the yeast in much the same way, resulting in the formation of considerable quantities of carbon dioxide, which, in escaping through the dough, cause it to become porous and light.

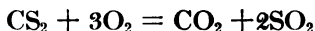
II. *Chemical Aeration, and Baking Powders.*—The chief problem in the leavening of dough is to obtain a sufficient quantity of carbon dioxide. It has been pointed out in the preceding pages that carbon dioxide is set free by treating a carbonate with an acid. All baking powders depend for their efficiency upon the liberation of carbon dioxide through the interaction of a carbonate and an acid, or an acid salt. They usually contain a third substance which is entirely inactive, and which serves to keep the active ingredients dry. There are two chief types of these powders:

1. One variety is made of sodium bicarbonate, potassium hydrogen tartrate (cream of tartar), and starch. The reaction which takes place, when a bit of the powder is moistened, may be expressed by the graph,

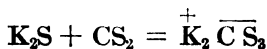


2. The second variety is made of sodium bicarbonate, primary calcium phosphate, and a neutral substance. The action of this powder is fundamentally the same as that of the first variety.

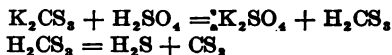
243. Sulphur Derivatives of Carbon.—Carbon forms a number of sulphur compounds, of which the bisulphide is the most important. Carbon bisulphide, CS_2 , discovered by Lampadius in 1796, is prepared by throwing sulphur upon charcoal which is heated to redness, and condensing the gas to a liquid. It is also prepared by an electrothermal process. Carbon electrodes, surrounded by lumps of coke, are set into the cup of an electric furnace. The cup is then filled with charcoal, sulphur is introduced, and the current is turned on. Enough heat is generated to vaporize the sulphur, which unites with the hot carbon, forming carbon bisulphide. It is a colorless, heavy, strongly refracting liquid which, when perfectly pure, has an agreeable odor like chloroform. It is readily inflammable, igniting at a low temperature and burning with a pale blue flame:



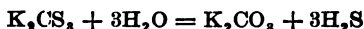
Commercial carbon bisulphide has a nauseating odor, which is due to the presence of certain impurities. Unlike carbon dioxide, it is a strong endothermic compound, its heat of formation being -26 Cal. It is extensively used as a solvent for fats, resins, phosphorus, oils, etc., which do not dissolve readily in water, alcohol, or other ordinary solvents. It resembles carbon dioxide in that it possesses the character of a weak acid anhydride. Thus, it combines with the sulphides of potassium or sodium, forming a salt of the general type, M_2CS_3 :



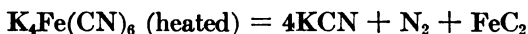
244. Sulphocarbonic Acid, H_2CS_3 , is analogous to carbonic acid in structure and deportment. When a sulphocarbonate in solution is acidified with a strong acid, free sulphocarbonic acid separates as a reddish-brown oil, but it is so very unstable that it decomposes readily into hydrogen sulphide and carbon bisulphide;



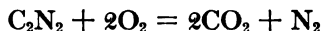
Carbon bisulphide may be viewed, therefore, as sulphocarbonic acid anhydride. Its salts, the sulphocarbonates, are less stable than the corresponding carbonates. Thus, a solution of potassium or sodium sulphocarbonate is decomposed upon boiling into a carbonate and hydrogen sulphide;



245. Cyanogen, C_2N_2 (also written CN), was discovered by Gay-Lussac in 1815. The union of the carbon and nitrogen is effected by indirect means, for they do not possess any direct affinity. When, however, organic compounds containing nitrogen and carbon, e.g., horns, hoofs, hair, blood, etc., are fused with potassium carbonate and iron, a peculiar compound (known as yellow prussiate of potash, $\text{K}_4\text{Fe}(\text{CN})_6$) is formed, in which the iron and cyanogen are acting together as a *negative radical*. When this salt is heated strongly, it is decomposed into nitrogen, iron carbide, and potassium cyanide;

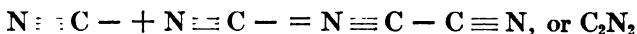


Cyanogen is a colorless gas, with an odor resembling that of peach blossoms. It dissolves in about one-fourth its volume of water. It is combustible, burning in the air with a characteristic violet-blue flame;

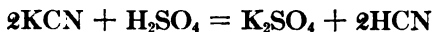


Nascent cyanogen consists of the single radical, CN. This is, however, an unsaturated compound, as may be seen from its structure, $\text{N} \equiv \text{C} -$. Like all such groups, it cannot

persist in the free state. It combines with itself to form a double molecule, C_2N_2 , or dicyanogen;



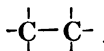
It is a negative radical, combining with bases to form salts, the cyanides, which are similar to the corresponding halogen derivatives. When one of these salts is treated with a strong acid, the corresponding salt of that acid is formed and hydrogen cyanide is set free;



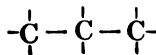
246. Hydrogen Cyanide, HCN, also called hydrocyanic or *Prussic Acid*, is a colorless, mobile liquid which boils at 26° , and is extremely poisonous. It is found in combination in the bitter almond, in the leaves of the cherry, laurel, etc. It dissolves readily in water, forming a clear liquid which gives a feeble acid reaction. It is monobasic, forming with most bases stable salts, uniformly poisonous, which find a limited use in the arts, and in medicine.

OTHER COMPOUNDS OF CARBON

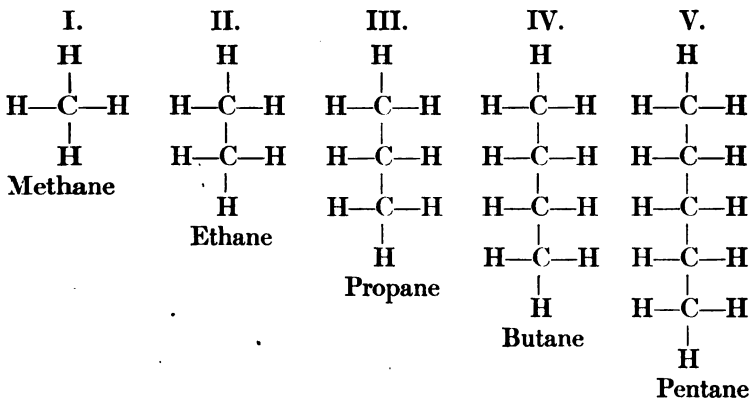
247. Ethane, Propane, Etc.—When *two* carbon atoms unite, there are six bonds remaining which must be combined;



By combining the six bonds with six hydrogen atoms, C_2H_6 is formed. This compound, called *ethane*, is a colorless, combustible gas which is always formed during the destructive distillation of coal. It burns with a pale blue flame. When *three* carbon atoms are bound into a chain by four bonds, there are (or may be) eight bonds which must be combined;

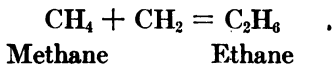


By combining these eight bonds with eight hydrogen atoms, C_3H_8 is formed. This compound, called *propane*, is a colorless and combustible gas, burning with a flame more luminous than that produced by ethane or methane. The derivation of these, and some other similar compounds, is shown by the following graphs;



HYDROCARBONS

It will be observed that the formula of each of the above compounds (called hydrocarbons) is the one that precedes it with CH_2 added. Thus,



It is also to be noted that the formulas contain twice as many hydrogen atoms, plus two, as there are carbon atoms. Thus pentane contains five carbon atoms, and $5 \times 2 + 2 = 12$ is the number of hydrogen atoms which it contains. Hence the general formula for the series is $C_nH_{(2n+2)}$, in which n is the number of carbon atoms in the compound. A large number of the compounds of this series are known. The following table includes some of the more important:

TABLE XXIII

NAME	FORMULA	BOILING POINT	SPECIFIC GRAVITY
Methane	CH_4		
Ethane	C_2H_6		
Propane	C_3H_8		
Butane	C_4H_{10}		
Pentane	C_5H_{12}	38°	0.620
Hexane	C_6H_{14}	70°	0.660
Heptane	C_7H_{16}	98°	0.690
Octane	C_8H_{18}	123-125°	0.706
Nonane	C_9H_{20}	148-150°	0.741
Decane	$\text{C}_{10}\text{H}_{22}$	171-173°	0.757
Undecane	$\text{C}_{11}\text{H}_{24}$	180-182°	0.765
Dodecane	$\text{C}_{12}\text{H}_{26}$	196-200°	0.774
Tridecane	$\text{C}_{13}\text{H}_{28}$	218-220°	0.792
Tetradecane	$\text{C}_{14}\text{H}_{30}$	236-240°	0.809
Pentadecane	$\text{C}_{15}\text{H}_{32}$	258-262°	0.825
Hekdecane	$\text{C}_{16}\text{H}_{34}$	278-280°	

248. Petroleum and Its Products.—The hydrocarbons have been obtained chiefly from petroleum by fractional distillation. When crude petroleum is distilled for *commercial* purposes, the product is collected within distinct zones of temperature. These zones, and the products which are obtained within them, afford the basis for the following table:

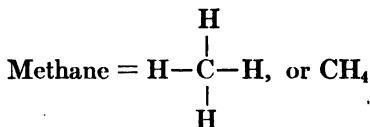
TABLE XXIV

ZONE	LOWER LIMIT	UPPER LIMIT	PRODUCT
1.	50°	60°	Petroleum ether
2.	60°	80°	[Petroleum, benzine, Gasoline
3.	80°	120°	Ligroine, Naphtha
4.	120°	150°	Cleansing oils
5.	150°	300°	Kerosene
6.	270°	310°	Lubricating oil
7.	300°	—	Paraffin, vaseline

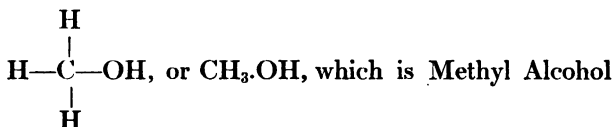
These commercial products are *mixtures* and not simple compounds.

ALCOHOLS

249. A very interesting relation obtains between the hydrocarbons given in Table XXIII and the alcohols. An alcohol may be viewed as a hydrocarbon in which one or more hydrogen atoms have been replaced by the hydroxyl group, OH. Thus, methane yields methyl alcohol;



Replacing one atom of H by OH, we have



250. Monatomic and Diatomic Alcohols.—When one hydrogen in a hydrocarbon molecule is replaced by an hydroxyl, the resulting alcohol is said to be monatomic. If one atom of hydrogen in ethane is replaced by an hydroxyl, *ethyl* or *grain alcohol*, $\text{C}_2\text{H}_5.\text{OH}$, is formed. When two hydroxyl groups are substituted for two hydrogen atoms in a hydrocarbon molecule, diatomic alcohol is formed. Thus, in propane we may have formed $\text{C}_3\text{H}_7(\text{OH})_2$, or diatomic *propyl alcohol*. These alcohols, therefore, have the general formula, $\text{C}_n\text{H}_{2n+1}(\text{OH})_x$, in which n is the number of carbon atoms. Diatomic alcohols are sirupy liquids which possess a more or less pronounced sweetish taste. None of them is of commercial importance.

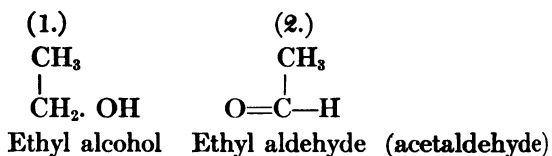
251. Triatomic Alcohols.—A triatomic alcohol is formed when three hydrogen atoms of a hydrocarbon molecule are replaced by three hydroxyl groups. Thus, $\text{C}_3\text{H}_7(\text{OH})_3$ is

formed when such a substitution is made in propane. This alcohol is the *glycerine* of commerce

Glycerine, first prepared by Scheele in 1799, is a constituent of all fats, and is always formed in small quantities during the alcoholic fermentation of sugar. The principal commercial supply is prepared by heating tallow or palm-oil to 280° - 315° , and distilling it in a current of superheated steam. The glycerine, which results from the decomposition of the fat, distills over with the steam, and is then purified. Its properties and uses are well known. The other triatomic alcohols possess little commercial value.

ALDEHYDES

252. When a primary alcohol is treated with a gentle oxidizing agent, two of its hydrogen atoms are withdrawn by the oxygen of the oxidizing agent, and there results a compound known as "aldehyde." This process may be seen in the oxidation of ethyl alcohol.



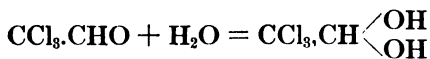
253. Properties of Aldehydes.—Aldehydes are mostly colorless gases or liquids which have a penetrating, suffocating odor, and their vapor is usually very irritating to the eyes and lungs. They are powerful reducing agents. This property may be illustrated by the following experiment:

EXPERIMENT 70. Introduce three cc. of an ammonia-silver solution (see Appendix) into a test tube, add 0.5 cc. of formalin, and heat the mixture in a water-bath. A beautiful mirror should be formed. There are two aldehydes which pos-

sess considerable commercial importance, formaldehyde and chloral.

254. Formaldehyde, $\text{H}\cdot\text{CHO}$, is prepared by leading a mixture of air and the vapor of methyl alcohol over a hot copper spiral, and collecting the product in water. It is a colorless gas whose water solution is pungent and suffocating. A water solution containing approximately 40 per cent of formaldehyde is called "formalin." It is rapidly fatal to bacteria and is, therefore, admirably adapted to disinfecting houses where there has been contagious disease. This may be conveniently done by saturating a cloth with the formalin solution and suspending it for twelve hours in the closed room. Tablets containing formaldehyde may be obtained from any druggist, and are very convenient for disinfecting large rooms. They should be placed in a tin pan, or other metallic vessel, and vaporized over an alcohol or gas flame. The room to be disinfected should be closed tightly and the vapor should be allowed to remain for twelve hours. This is usually very effective, and commends itself because of its simplicity.

255. Chloral, $\text{CCl}_3\cdot\text{CHO}$.—This well-known substance may be viewed as acetaldehyde, $\text{CH}_3\cdot\text{CHO}$, in which the hydrogen atoms in the CH_3 group have been replaced by chlorine. It is prepared by conducting dry chlorine gas through ethyl alcohol until the vapor of hydrochloric acid is no longer given off. It combines with water, forming chloral hydrate;

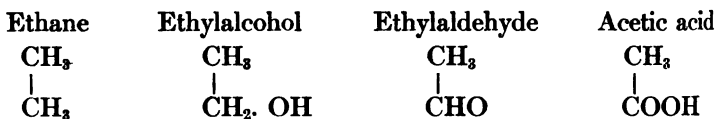


256. Chloral Hydrate forms colorless, monoclinic crystals which are stable under ordinary conditions. It has a

peculiar, penetrating odor, and a characteristic flavor. It is esteemed in medicine because of its soporific qualities.

ORGANIC ACIDS

257. Composition of Organic Acids.—An organic acid represents the third stage in the oxidation of a hydrocarbon. Otherwise stated, the acid is formed when the aldehyde group, CHO, is oxidized to COOH. The action of the whole process may be epitomized in the transformation of ethane to acetic acid. These stages are expressed by the formulas,



Indeed a monobasic organic acid may be viewed as the corresponding hydrocarbon in which a CH_3 group has been oxidized to COOH. These acids, therefore, possess the general formula, $\text{C}_n\text{H}(2n + 1). \text{COOH}$. Several of them are of great commercial importance, especially acetic acid.

258. Acetic Acid, $\text{CH}_3.\text{COOH}$, or $\text{HC}_2\text{H}_3\text{O}_2$, is formed by the oxidation of more complex organic compounds, especially by the oxidation of ethyl alcohol. It is a colorless liquid which solidifies below 16° to a crystalline mass, called "glacial" acetic acid. It mixes with water in all proportions. Thus vinegar is essentially water which contains approximately 4 per cent of its weight of acetic acid.

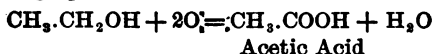
259. Preparation of Vinegar.—There are two common methods of preparing vinegar:

1. Apples or other fruits rich in sugar are crushed, the juice is pressed from the pulp and drained off, and the resulting liquid,

which contains the sugar in solution, is allowed to undergo the alcoholic fermentation;



The alcohol is then acted upon by a minute organism called *mycoderma aceti* (masses of them are known as *mother of vinegar*), which oxidizes the alcohol to acetic acid. The process in its simplest form is expressed by the graph,



The quantity of acetic acid does not rise above 15 per cent, for the reason that the organisms are killed when the acid attains that strength. Such a vinegar is usually of a reddish color and possesses a sour taste.

2. The second process, called the "rapid process," consists in oxidizing dilute alcohol to acetic acid in an apparatus especially adapted to the purpose. Such an apparatus is shown in Fig. 59. The cylinder A is usually about eight feet high and five feet in diameter. False and perforated bottoms B and B' are placed about two feet from each end, and the intervening space is then filled with beech shavings or sawdust, which is moistened with vinegar. This has for its purpose the "seeding" of the shavings with the spores of *mycoderma aceti*, which are always present in normal vinegar. The upper surface of the perforated bottom is usually covered with a coarsely woven cloth. Dilute ethyl alcohol is poured into the cask at D. In passing through the cloth, it is broken into a fine spray, whereby it is distributed more uniformly through the shavings and comes more uniformly into contact with the *mycoderma aceti* which infest them. There must be a free circulation of fresh air within the cask. This is secured by openings *a a a* at the base of the cask, and immediately below the level of the lower false bottom. The temperature within the cask must be kept between 27° to 35°. If it fall below 27° the organisms become

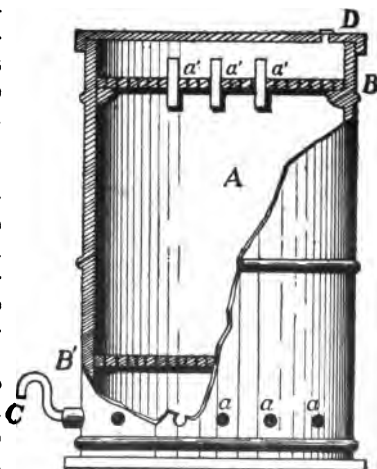


FIGURE 59

less active, thereby lessening the oxidation of the alcohol; if the temperature rises above 35° , alcohol will be lost by evaporation. The temperature without the cask should be approximately 20° . This will insure a free circulation of air within the cask, for the warm air rises up through the canals $a' a' a'$, and escapes, while the cooler air comes from below to supply its place. When the alcohol collects at the bottom, it is drawn off at C and again put through the apparatus. This treatment usually oxidizes about 80 per cent of the alcohol.

260. Salts of Acetic Acid.—This acid contains only one replaceable hydrogen atom. It forms salts of the general type, $M.C_2H_3O_2$, which are fairly stable compounds under ordinary conditions, but are decomposed by a strong heat. The oxide of the base is then usually formed, carbon is set free, and volatile products are given off. Some of the acetates are of considerable commercial importance.

1. *Lead Acetate*, $Pb(C_2H_3O_2)_2$, is a white crystalline solid which possesses a sweetish taste, hence the name "sugar of lead." It is used to a limited extent in medicine, in dyeing, and in preparing yellow paint.

2. *Copper Acetate*, $Cu(C_2H_3O_2)_2$, is a blue-green solid. Its basic form, $[2Cu(C_2H_3O_2)_2 + CuO]$ called "verdigris," is used to some extent in making blue paint, and as a caustic in the treatment of ulcers and chronic sores.

3. *Paris Green* is a double salt, consisting of copper arsenite and copper acetate. It is used as a pigment in the manufacture of wall-paper, and as a germicide and insect destroyer. It is a deadly poison.

261. Palmitic Acid, $C_{15}H_{31}.COOH$, occurs in combination with glycerine in palm-oil and other fats. It is a white, soft solid, "fatty" to the touch. It is insoluble in water, but dissolves readily in hot alcohol, ether, chloroform, glacial acetic acid, or hot potassium or sodium hydroxide. It is a monobasic acid, and its salts, the palmitates, are, with the exception of potassium and sodium palmitate, insoluble in

water. Its sodium and potassium salts have great commercial importance.

262. Stearic Acid, $C_{17}H_{35}COOH$, is found combined with glycerine in all varieties of animal fat. The pure acid is a white, crystalline mass which melts at about 70° . It is insoluble in water, and deports itself like palmitic acid toward other solvents. It is a monobasic acid which forms stable salts very similar in their physical and chemical properties to the corresponding salts of palmitic acid.

263. Oleic Acid, $C_{17}H_{33}COOH$, is found combined with glycerine in nearly all fats. It is especially abundant in heavy oils, such as olive, almond, whale, and seal oils. The chemically pure acid is a colorless, odorless, and tasteless oil, which boils at about 285° , and crystallizes at $+4^{\circ}$. On exposure to the air it absorbs oxygen rapidly and assumes in consequence a yellow color and a sharp, rancid taste. It is monobasic and forms, with the metals, salts which are similar to the corresponding salts of palmitic and stearic acids. Its alkali salts are the only ones which dissolve readily and completely in water. One of its most important salts commercially is lead oleate, $Pb(C_{17}H_{33}COO)_2$, extensively used in the preparation of lead plasters, etc.

FATS

264. Composition of Fats.—Palmitic, stearic, and oleic acids are of especial interest in that they enter into the composition of nearly all common fats.

These fats are the glyceryl salts of the fatty acids; i.e., the tribasic glyceryl group C_3H_5 has replaced three positive hydrogen atoms in

three molecules of each acid. The formation of such molecules may be expressed by the graphs,

1. $C_3H_5(OH)_3 + 3 C_{15}H_{31}.COOH = C_3H_5(C_{15}H_{31}.COO)_3 + 3H_2O$
 Glycerine Palmitic acid Glyceryl palmitate (Tripalmitine)
2. $C_3H_5(OH)_3 + 3 C_{17}H_{33}.COOH = C_3H_5(C_{17}H_{33}.COO)_3 + 3H_2O$
 Glycerine Stearic acid Glyceryl stearate (Tristearine)
3. $C_3H_5(OH)_3 + 3 C_{17}H_{33}.COOH = C_3H_5(C_{17}H_{33}.COO)_3 + 3H_2O$
 Glycerine Oleic acid Glyceryl oleate (Trioleine)

The physical attributes of a fat depend largely upon the relative proportions in which these three salts are present. Fats in which tripalmitine and tristearine are present in large proportion are usually hard, very white, and do not change readily in the air. Beef and mutton tallow, hog's lard, and cocoa butter are good examples of such a fat. Those fats in which trioleine is the predominating constituent are usually soft or wholly fluid, of a pale yellow or brown color, and are more or less easily decomposed on exposure to the air. Olive, whale, and cod-liver oils are representatives of such a fat. While the bulk of a fat is made up of tripalmitine, tristearine, and trioleine, its flavor and palatableness depend largely upon the glyceryl salts of the fatty acids, which have a smaller number of carbon atoms. Chief among these are

Glyceryl butyrate..... $C_3H_5(C_3H_7.COO)_3$
 " valerianate..... $C_3H_5(C_4H_9.COO)_3$
 " capronate..... $C_3H_5(C_5H_{11}.COO)_3$
 " caprylate..... $C_3H_5(C_7H_{15}.COO)_3$

These salts are more or less volatile, and possess an agreeable flavor and a pleasant aroma. Any fat which contains them in appreciable quantities has found favor as an article of diet. Ordinary butter is perhaps the best representative of such a fat.

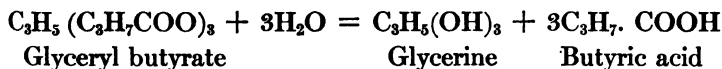
265. Butter.—Butter differs from all other ordinary fats in that about one-tenth of its fat is made up of the glycerids

of the lower fatty acids, the remaining nine-tenths of the fat consisting of tripalmitine, tripoleine, tristearine. Table XXV contains the analysis of an average sample.

TABLE XXV

	PER CENT
Water.....	13.00
Fat	85.00
Casein	0.50
Milk sugar.....	0.50
Salt.....	1.00

The superiority of a butter depends largely upon the quality of the cream from which it is prepared, and its method of preparation. The excellence of creamery butter is due largely to the fact that it is manufactured from fresh cream, i.e., cream which has not been allowed to sour. Fresh cream yields a little less butter than the sour cream, but the product is more palatable and less likely to become rancid. The rancidity of butter is due to the fact that parts of the glycerids, especially of the lower acids, have been broken up into glycerine and the free fatty acids;



It is to the presence of the free acids, especially butyric acid, that rancid butter owes its disagreeable flavor. When butter is prepared from sour cream, some of the casein (clabber) remains with the fat. The casein is infected with bacteria, which decompose the fats into glycerine and the free acid.

266. Oleomargarine.—Oleomargarine, which, in all of its essential attributes, is a perfect substitute for common butter, is made of animal fat, and cream. Formerly beef-tallow was used almost exclusively. At present lard is largely used. The

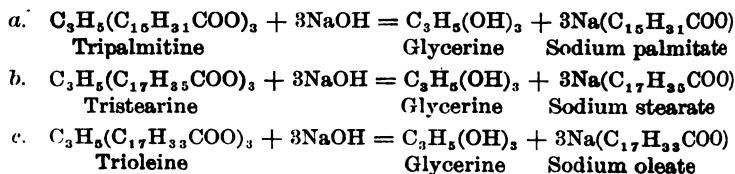
details of the process by which an artificial butter is prepared depend upon the manufacturer, although the same fundamental steps are employed by all. A firm in Frankfort, Germany, uses the following process:

The lard is melted and kept liquid for many hours, to allow any impurities to sink to the bottom of the containing vessel. The clear upper liquid is then drawn off into vessels which are maintained at such a temperature that the tripalmitine and the tristearine separate as a crystalline mass, the more fluid trioleine remaining in solution. The crystalline mass is then subjected to high pressure, by which most of the trioleine (mixed with some tripalmitine and tristearine) is separated and drawn off into large vats. The hard crystalline cakes, consisting of tristearine and tripalmitine, which remain in the presses supply a material from which candles are made. The trioleine is then mixed with about 20 per cent of its volume of sweet cream, churned thoroughly, and the mixture is run into vats of cold water, where it solidifies into snowy flakes. These flakes are then run between large rollers to expel the water, after which they are colored with turmeric, Victoria, or Orleans yellow.

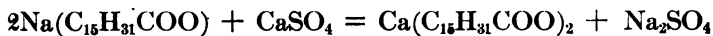
It will thus appear that oleomargarine is essentially butter, from which much of the tripalmitine and tristearine have been removed. When such a butter is prepared properly from pure fat, it is palatable and perfectly wholesome. The following is the analysis of a sample purchased in the Indianapolis market:

Water	Fat	Casein	Milk sugar	Ash
10.2	85.52	1.4	0.3	2.50

267. Soap.—Soap consists of the sodium or potassium salts of the fatty acids, especially oleic, stearic, and palmitic. When their glyceryl salts are heated in a water or alcoholic solution of sodium or potassium hydroxide, they are decomposed into glycerine and the corresponding salt of the alkali;



The process of decomposing a fat into glycerine, and the free acid or its salt, is called "saponification." The quality of a soap depends, first, upon the nature of the raw materials, and, second, upon the method of its preparation. There are, in fact, only two important varieties, the potassium soaps and the sodium soaps. When potassium hydroxide is used to effect the saponification of the fats, the resulting soap is soft and smeary. When sodium hydroxide is used, soap is obtained which is hard and brittle. Sodium soaps can take up from 50 to 60 per cent of their weight of water, and yet remain hard and firm. All soaps of good quality dissolve readily and completely in warm water to a clear fluid which foams when shaken. When a little soap is dissolved in much water, it is decomposed into acid salts, and free potassium or sodium hydroxide (Krafft). This fact affords some explanation of its cleansing power. When the object to be cleansed is rubbed or warmed with the soap solution, the free alkali combines with any grease which may be present to form soluble sodium or potassium salts. It follows that a soap's effectiveness depends upon the presence of this free alkali. A soap loses much of its effectiveness when "hard" water is used. This finds a simple explanation in the fact that such water contains soluble salts of calcium or magnesium. The effect of such a salt upon a soap solution is shown in the equation,



The products of this reaction are both ineffective; the calcium palmitate separates as a white, curdy mass; the sodium sulphate remains in solution as an indifferent salt, for it possesses no cleansing power. A soap becomes effective in hard water only after the calcium and magnesium salts have been precipitated. In order to understand this, dissolve a small quantity of finely divided soap in hot water and add a few cc. of

a calcium or magnesium sulphate solution. A white curdy mass will be formed.

268. Preparation of Soap: Laboratory Method.—

I. *Preparation of soda soap.* EXPERIMENT 71. Put 15 gm. of tallow or lard in a 800 cc. Erlenmeyer flask, add approximately 100 cc. of sodium hydroxide solution (4 gm. of NaOH in 150 cc. of water); heat the mixture over a wire gauze until it ceases to foam; then add an equal volume of a saturated solution of common salt and let the mixture stand until it separates into an upper zone or crust, and a lower more or less colorless liquid. The crust is a mixture of soda-soap and unsaponified fat; the lower liquid contains salt, glycerine and other impurities.

Drain off the liquid, add 80 cc. of the sodium hydroxide solution to the crust in the flask, and heat as above directed until the mixture becomes adhesive. Then pour it into an open dish and let it solidify. The product should have the essential qualities of hard soap.

II. *Preparation of glycerine soap.* EXPERIMENT 72. Put 10 gm. of castor oil and 5 cc. of glycerine in a large flask, add 120 cc. of sodium hydroxide solution (6 gm. NaOH in 75 cc. of alcohol and 75 cc. water) and heat the mixture until it ceases to foam and becomes more or less pasty. Pour the clear liquid into an open vessel to cool. It should form a solid and more or less translucent mass which has the essential properties of a glycerine soap.

269. Preparation of Soap: Commercial Method.—

The essential problem in making hard soaps is to effect a complete saponification of the fat without using an excess of alkali, and to effect a separation of the glycerine and other impurities from the soap.

Process.—A weighed quantity of fat is put into the large kettle B (Fig. 60), about one-fourth of the quantity of sodium hydroxide (weak lye) necessary to completely saponify it is added, and steam is turned on from the pipe C or D, and the mixture boiled for about four hours. When the contents become uniformly mixed, an additional quantity of lye is run in, and the mixture is heated until it becomes elastic. A strong solution of common salt is then added, the boiling is stopped, and the kettle is let stand for several hours. The contents of the kettle separates into two portions, the upper consisting of soap (which holds some water and a little unsaponified fat); and the lower consist-

ing principally of water which contains salt, glycerine and all impurities. The water is then drawn off through the pipe A. The rest of the

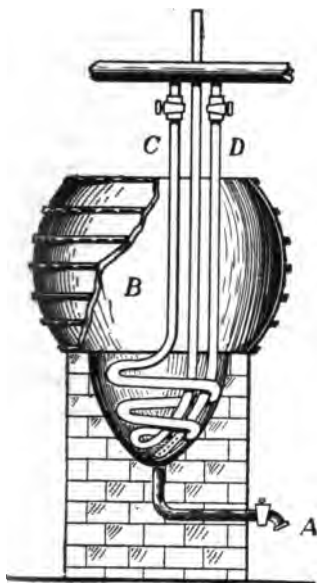


FIGURE 60

soda necessary to completely saponify the fat is added, and the mixture again boiled until the soapy particles distributed through the fluid, coalesce into a pasty mass, resting on the surface of the water. In some cases water or very weak lye is now added, and the mixture allowed to stand until complete separation of the curd takes place. It is then

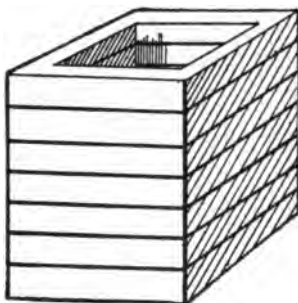


FIGURE 61

transferred to cooling frames (Fig. 61), and allowed to stand until it "sets" to a hard mass, after which it is cut into cakes by forcing the large block against a wire screen made of the strongest steel wire.

When a quantity of free alkali becomes enclosed between the particles of soap, it collects into drops as the stock solidifies in the frames, and gives to the cakes or bars a peculiarly mottled appearance. The characteristic green and red streaks in Castile soap are made by adding a little ferrous sulphate to the stock before it solidifies. The yellow laundry soaps are made from tallow and rosin, the latter being added to the stock before the last boiling. The pinic acid (p. 288) in the rosin combines readily with the alkali, forming a soluble rosin soap.

Soaps made by this process are adapted to general domestic use, but they are not suitable for toilet purposes because they

usually contain some free alkali, which is irritating to sensitive skins. The manufacture of toilet soaps involves the same important chemical and physical processes used in making the laundry soaps above described, but the raw materials are of a finer quality, and the greatest care is taken to mix the ingredients in exactly the right proportions. The stock soap or curd is then treated in various ways to give to it certain attractive qualities. Thus, in preparing some of the fine French soaps, the stock soap is cut into very thin slices, warmed at a low temperature until most of the water is expelled, and then ground to a very fine powder. To this powder the perfume and coloring ingredients are added, and the mixture is moulded into long bars in a pressure cylinder. These bars are then cut into the proper lengths and stamped into cakes. A high polish is given to the cakes by rubbing them with a cloth dipped in alcohol.

THE CARBOHYDRATES

270. Composition of Carbohydrates.—Carbohydrates are made up of carbon, hydrogen, and oxygen, with the hydrogen and oxygen in the proportion to form water; hence the name, “carbohydrates.”

They are found in fruits, cereals, vegetables, legumens, etc. The starches and sugars belong to this series. Table XXVI includes some of those which are of special importance.

TABLE XXVI

$C_6H_{12}O_6$	$C_{12}H_{22}O_{11}$	$C_{18}H_{32}O_{16}$	$C_6H_{10}O_5$
Grape sugar....	cane sugar....	melitose.....	cellulose.....
Fruit sugar.....	milk sugar....	stachyose.....	starch.....
Glucose.....	maltose.....		dextrin.....
etc.	etc.	etc.	glycogen, gums etc.

271. Properties of the Carbohydrates.—Carbohydrates form amorphous or crystalline solids which are stable under ordinary conditions, but are decomposed by heat or concentrated sulphuric acid into charcoal, water, and other products. The starches and sugars serve as raw materials from which much of our food is prepared. Sugar is obtained chiefly from the sugar beet and sugar cane. The composition of the sugar beet may be seen in the following table.

TABLE XXVII

SUGAR BEET	WATER	ALBUMEN	GUM	SUGAR	FIBER
Sample No. 1	84.15	0.80		13.01	1.05
“ “ 2	82.35			11.45	
“ “ 3	81.15	1.01		12.33	0.75
“ “ 4	80.92	1.04	1.00	12.11	

272. Sugar Making.—In the United States the juice of the sugar cane is the chief source of cane sugar. The following table contains the analysis of four samples of the fresh juice of the cane.

TABLE XXVIII*

No.	TOTAL SOLIDS	SUCROSE $C_{12}H_{22}O_{11}$	GLUCOSE $C_6H_{12}O_6$	ALBUMEN
1.....	16.54	13.05	0.67	0.19
2.....	20.90	19.20	0.66	1.04
3.....	20.20	18.50	0.14	1.56
4.....	21.40	20.60	0.08	0.71

The problem of the refiner is to separate the cane sugar from the albumen, glucose, cellulose, and such organic acids

* Data from Sattler.

as may be present, so that the sugar will crystallize. The process by which this is accomplished is divided into two steps:

- 1). The preparation of the raw sugar.
- 2). The refining of the raw sugar.

1). *Preparation of Raw Sugar.*—The canes are first stripped of their leaves, and dusted. The clean stalks are then run between large iron rollers under great pressure. This serves to squeeze out about 90 per cent of the juice. The juice is run into a pan, about four ounces of calcium oxide per gallon are added to neutralize the organic acids, and the whole is then heated gently.* This brings to the surface a thick scum of coagulated albumen, suspended fibers, and insoluble lime salts of the organic acids. The first scum is removed, and the boiling continued until a scum ceases to form. The next step consists in concentrating the juice to a thick syrup in "vacuum-pans." The "vacuum-pans" consist of a mechanical arrangement by which the juice may be concentrated under reduced pressure at a temperature of 130° - 170° , whereas the open pan requires a temperature of approximately 250° . Such a high heat (250°) decomposes much of the sugar into brown, gelatinous products which greatly retard the subsequent crystallization. When the concentration reaches the point where the sugar begins to crystallize, the juice is run into separate vessels, where it remains until the crystallization is complete.

The next problem is to separate the raw crystals, which are of a light brown color, from the sticky, brown liquid which surrounds them. This is now done by whirling the mass in a centrifugal machine. This machine consists, in its simplest form, of a drum whose sides are thickly perforated

* If these acids are not neutralized, they start a fermentation which changes the cane sugar to glucose, a compound which does not crystallize. An excess of the lime must be avoided or it will decompose the glucose, forming dark-colored products which are detrimental.

with very fine holes. This drum is set into another whose sides are solid, and whose diameter is several inches greater than that of the first. The whole is so arranged that the smaller drum may be rotated about 1,000 times a minute, the larger one remaining fixed. The crystalline mass is placed in the inner drum, and the drum is rotated rapidly. The syrup flies off through the small holes, and, from the space between the drums, it runs off into a receiver. The crystals which remain in the drum constitute the "brown sugar" of commerce, and are packed into sacks or hogsheads and shipped to the refineries.

2). *Refining the Raw Sugar.*—This process consists in removing the coloring matter from the raw sugar and crystallizing the colorless liquid. This is effected by the appliances shown in Fig. 62.

The raw sugar is placed in the tanks A A A A, which are capable of holding about 10 tons at a time, and dissolved in boiling water. The solution is then run through a coarse strainer, after which it is pumped into the receiving tanks B B. where it is boiled and agitated for about 20 minutes. It is then run into the bag filters C C. These bags are made of thick cotton cloth and are about 4 feet long and only a few inches wide. These filters remove the fine suspended particles, scum, etc. The solution passes from these to a second set

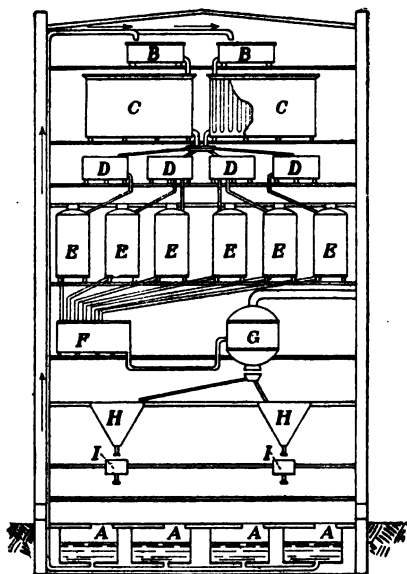


FIGURE 62

of storage tanks D-D, thence into the clarifiers E-E. These are immense iron cylinders, each of which contains about 30 tons of boneblack. The syrup percolates slowly through the bone-black filter, and drains into the storage tank F. It is now perfectly clear, but very dilute. It is then concentrated in the vacuum-kettle G, drained into coolers H H, where it crystallizes, and the crystals are separated from the adhering liquor by the centrifugal machines I I.

The crystals or granules are of a pure white color, and make up the granulated sugar of commerce. The liquor which is thrown from the centrifugal machines I I, is known in the trade as "Golden Syrup."

273. Manufacture of Glucose.—Glucose may be made from starch by heating it for some time with a dilute acid, usually sulphuric. The apparatus consists usually of a very large wooden or copper boiler which is supplied with steam pipes for boiling the contents, and paddles for stirring. The walls of the vat are sufficiently strong to withstand a pressure of about 100 lbs. per square inch. A foot or two of water is first run into the boiler, and to this is added about half a pound of concentrated sulphuric acid for each 100 lbs. of starch. This is heated to the boiling point, and the starch, previously mixed with water, is pumped into the acid solution slowly, so that the boiling is not checked. The boiler is securely closed, and the steam pressure is brought up to about 75 lbs. per square inch, and the boiling is continued for from 10 to 40 minutes. The reaction taking place within the boiler may be expressed by the graph,



The product is then run into open vats, and any excess of acid is neutralized with marble-dust. After the separation of the insoluble calcium sulphate, the clear liquid is drained off,

filtered, decolorized in boneblack filters, condensed in vacuum pans, and again filtered.

If the product will not crystallize, the thick syrup, which is a mixture of dextrin and grape sugar, is sold to the trade and is called "glucose." If it forms a crystalline mass, it is sold as "grape sugar."

274. Properties of Grape Sugar.—This form of sugar is a constituent of the juices of ripe grapes, figs, cherries, plums, etc. It is not so sweet as cane sugar, it readily undergoes fermentation, and it is broken up by yeast into ethyl alcohol and carbonic acid anhydride. When it is heated to about 400° , it is converted into a brown substance called caramel.

Caramel is neither sweet nor capable of fermenting. It dissolves readily in water, forming a brown liquid, and is much used by confectioners as a coloring matter.

275. Starch.—This important carbohydrate is found in the stems, stalks, seeds, fruits, and leaves of plants. It is found in abundance in wheat and other cereals, and in potatoes, rice, sago, tapioca, etc. Its presence in the different cereals may be seen from the following analyses:

TABLE XXIX*

	WHEAT	RYE	CORN	BUCKWHEAT	OATS	BARLEY
Water.....	13.37	13.71	14.21	13.31	7.95	14.05
Albumens.....	10.21	11.57	9.65	8.87	13.13	9.88
Fat.....	0.94	2.08	3.80	1.56	8.83	1.80
Carbohydrate...	74.71	69.61	69.55	74.25	66.33	66.75

Starch is a white powder which, when seen under the microscope, is found to be made up of fine oval grains. They

* Data from König. The analysis of each sample does not make up 100% because the percentage of ash was omitted.

are not soluble in water, but when they are suspended in it and the liquid is boiled, the grains swell and burst, and the contents dissolve to a large extent.

When starch is heated to 200° - 250° , it forms a solid sticky mass called *dextrin*, which is soluble in water. Mucilage and the various "library pastes" contain a high per cent of dextrin.

276. Starch, and Malted Foods.—When barley is moistened and allowed to remain in a warm atmosphere until it begins to germinate, a large percentage of the starch which it contains is transformed into a sugar called *maltose*, by the action of an unorganized ferment, *diastase*, which is found within the seed. This transforms the insoluble starch into the more soluble, and therefore more digestible, sugar. This fact is made use of in the preparation of many of our "predigested" breakfast foods. They are primarily a mixture of grains in which a part or all of the starch has been changed to sugar. The following analyses of breakfast foods will throw much light upon their preparation, and nutritive qualities.

TABLE XXX *

SAMPLE	Moisture	Fat	Ash	Albumen	Fiber	Dextrin	Starch	SUGAR
								Materials soluble in cold water
	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Grape Nuts	9.43	0.58	1.64	12.00	2.03	24.87	49.45	49.50
Force	11.92	1.27	2.75	11.56	2.60	14.48	55.42	29.60
Malta Vita	11.10	1.25	3.00	9.88	3.15	9.28	62.36	30.88
Malta Vita	6.00	1.63	2.33	8.47	2.70	14.04	56.41	Maltose 8.42
Ralston's Break- fast Food	13.02	1.54	0.78	12.50	1.68	2.63	67.86	7.50
Rollad Oats	11.21	7.21	1.68	12.69	3.14	3.58	60.49	6.19
Oatmeal	10.84	6.91	1.14	13.00	4.28		63.83	3.85

277. Baby Foods.—The artificial preparations which are sometimes given to infants are made up of cereals which have

* Canadian Government Report.

been modified in one of three ways: (1) by application of heat alone; (2) by digestion with malt or diastase; or (3) after the cereal is malted, by evaporation with cream or milk.

(1). *Foods Prepared by Heat Alone.*—The following infant foods belong to this class: Blair's, Schumacher's, and Robinson's foods, and Imperial Granum.

(2). *Malted Foods.*—These products are prepared by mixing wheat flour and malt with a little potassium bicarbonate, moistening with water, and heating at a fixed temperature for several hours. This suffices to change the starch in the flour into maltose and dextrin, both of which are soluble. Mellin's, Horlick's, and Moore's foods are representatives of this class.

(3). *Malted Foods and Cream.*—These foods are made from wheat or other flour. The flour is made into dough, baked, ground, malted, mixed with cream, and evaporated to dryness in a vacuum. These foods are, therefore, much richer in fat and albumen than the preceding. The chief representatives of this class are Malted Milk, Lactated Food, Nestle's Food, and Carnrick's Food.

The following analyses will show the class to which each belongs:

TABLE XXXI*

BABY FOODS	WATER	ALBUMEN	FAT	CARBOHYDRATES		ASH
				SUGAR	STARCH	
Nestle's ..	6.15	9.91	4.46	42.3	35.00	1.74
Mellin's...	6.87	8.95	0.34	61.47	18.84	2.94
Horlick's..	5.08	9.67	0.34	66.39	16.00	2.02
Neave's ..	4.27	13.20	1.70	4.71	74.14	1.09

The analysis shows clearly that Nestle's, Mellin's, and Horlick's are malted (the insoluble starch has been changed to soluble sugar). Neave's consists essentially of a cereal to which some form of albumen has been added.

* Data from König.

278. Cellulose.—Cellulose ($C_6H_{10}O_5$), is of plant origin. When pure it is a white, amorphous or fibrous mass which is insoluble in water, alcohol, ether, acids, and alkalis. It is a very stable substance under ordinary conditions, but at high temperature is combustible in atmospheric oxygen, burning with a luminous flame. When it is heated for many hours with dilute sulphuric acid, it takes up a molecule of water and forms grape sugar:



279. Uses of Cellulose.—Cellulose is of great commercial importance. Cotton and linen fibers are made of it. The length of its fiber, whiteness, durability, etc., make cotton a raw material of prime importance for the manufacture of thread, and various other things. Cellulose is the chief constituent of our writing and wrapping papers, as well as of many other varieties of articles which can be made from fiber or pulp.

280. Paper Making.—The sources of paper fiber in the United States are chiefly cotton, flax, hemp, wood, and straw. The chemical composition of the crude stuffs is very similar, as may be seen from the following analyses:

TABLE XXXII*

RAW FIBER	COTTON	FLAX	HEMP	WHEAT STRAW	BIRCH WOOD
Cellulose	91.15	81.99	77.13	46.60	55.52
Fat	0.51	2.37	0.55	1.49	
Aqueous Extract ..	0.67	3.62	3.45	8.07	2.65
Water	7.56	8.60	8.80	9.85	12.48
Ash	0.11	0.70	0.82	5.50	
Pectous substances.		2.72	9.25		
Non-cellulose				28.49	28.21
Resin					1.14

* Data from Müller.

The manufacturer has to free the cellulose from most of the other materials with which it is associated, and to reduce its fiber to a homogeneous pulp. The first problem is largely a chemical one, while the second calls for careful physical processes. The similarity in the composition of the raw materials shows that whatever material is employed, the fundamental processes must be the same. In making linen and cotton scraps and rags into writing paper, the process is as follows:

1. *Cleansing and Maceration.*—The material is cut into pieces about two inches square, after which it is freed from dust and dirt by mechanical means. It is then placed in a large spherical boiler, which is fitted with steam pipes for heating the contents. An alkali, such as calcium oxide, sodium carbonate, caustic soda, etc., is added, sufficient water is run in to make a strong solution of the alkali, and the contents are boiled for from two to six hours. When the boiling is finished, the alkaline liquor is drained off and the material within the boiler is rinsed with clean water. The boiling with an alkali dissolves and removes the fat, wax, dirt, etc. The material is then run into a washer or "breaker." This consists of a large box within which a heavy-toothed wheel travels for further cutting and macerating the material until it is reduced to a fine pulp. The pulp is at the same time floated in a rinsing water which flows slowly through the washer. The water not only washes the pulp, but it also makes it more homogeneous. When the pulp is thoroughly cleansed and mixed, it is run into a vat to be bleached. It is now called "half-stuff."

2. *Bleaching the Pulp.*—A clear solution of calcium hypochlorite is run in, containing about 4 lbs. of the hypochlorite for each 100 lbs. of the original material used. In some mills, sufficient sulphuric or hydrochloric acid is now added to liberate the hypochlorous acid, which bleaches more rapidly than its calcium salt (p. 194). The mixture is gently stirred for some hours, the time necessary to effect a good bleach depending largely upon the kind of raw material, the condition of the pulp, and the strength of the bleaching solution.

3. *Beating the Pulp.*—The bleached "half-stuff" is generally washed until the excess of bleaching powder and other soluble products are removed, and then it is run into the "beater." This machine is similar in construction to the washer, but it is better adapted to mixing the pulp more uniformly. The beater effects a complete separation of the individual fibers, which, at this stage of the process, are aggregated into masses. The "beating" of cotton and flax fibers may require ten hours. The beating process is very important and it

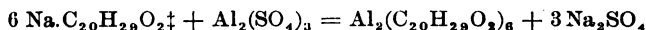
requires great skill to judge when it is properly done. A pulp which is not properly beaten will yield a paper which is wanting in evenness of texture and other good qualities. If it is over-beaten, it becomes too gelatinous. It is only for the thinnest varieties, such as tissue paper, that the pulp is thoroughly beaten.

4. *Sizing the Pulp*.—If the beaten pulp were made into sheets at this stage, it would yield a "blotting" paper. In fact, blotting paper is made of beaten pulp to which a little starch has been added for the purpose of binding the individual fibers together, and giving it a certain degree of toughness. Writing paper must be *hard* and *firm*. This property is imparted to it by certain chemicals called "sizing" agents. These are of great variety, and the chemical changes which they bring about are not well understood.

A "size" made of rosin and alum is very effective. Its action may in part be understood from the nature of the two compounds. Rosin is made up largely of pinic* acid, $C_{20}H_{30}O_2$, and this acid combines readily with the alkalis, forming the corresponding salts, which are soluble in water. In preparing the size (which is a pure rosin soap), the requisite quantities of sodium carbonate and rosin are mixed and boiled for three or four hours. On cooling, the size separates as a semi-solid, gelatinous mass.

The quantity of this size, which represents about 2 lbs. of the original rosin, is added to each 100 lbs. of the pulp when the beating process is perhaps two-thirds finished. The subsequent beating serves to mix the size and fiber very thoroughly†.

It must be apparent that since the pulp is about 95 per cent cellulose, and the size is soluble in water, a third substance is necessary to fix the rosin upon the pulp in an insoluble condition. Aluminium sulphate (alum) is generally used for this purpose. Its effect upon the size is similar to the action of calcium sulphate upon sodium stearate (p. 275). It may be expressed by the graph,



5. *Loading the Pulp*.—After the pulp has been treated with the alum size, a quantity of some inert mineral, such as calcium sulphate, kaolin, or magnesium silicate, is added to the contents of the beater. When kaolin is used, it is first finely powdered, mixed with water until a creamy liquid is obtained, and then strained into the pulp through a very fine sieve. The quantity of kaolin which is added varies from two to thirty per cent. The kaolin, or some other min-

*Bellstein gives to this acid the formula $C_{44}H_{64}O_5$, and calls it abietic acid.

† See C. F. Gross: Paper-making.

‡ Wüster uses Bellstein's formula for abietic acid, $C_{44}H_{64}O_5$.

eral, serves to fill up the pores of the paper. It also makes it less transparent and gives to it a more uniform surface.

6. *Calendering*.—This is a purely physical process. It must be seen to be understood.

When the web comes from the machine by which it is shaped, the surface of the paper does not possess the requisite polish. This polish is put on in several ways, one of which is called "friction-glazing." This consists in passing the paper between two rollers, one of which is large and the other small, the smaller one revolving at a much higher speed than the larger. This has the effect of imparting a gloss to the rosin and kaolin which surround the fibers. It is thus apparent that the size not only binds the fibers together, but it also gives a *firm texture* and a *glossy surface* to the finished product.

281. Modifications of Cellulose.—Parchment, and a smokeless powder are also prepared from cellulose.

1. *Parchment*.—When filter paper, which consists essentially of cellulose, is moistened with dilute sulphuric acid and then washed carefully, it assumes a peculiarly hard, semi-transparent appearance. The product is known commercially as "vegetable parchment."

EXPERIMENT 73. Mix 65 cc. of concentrated sulphuric acid with 500 cc. of water and allow the mixture to cool. Immerse a strip of filter paper in the solution, and allow it to remain for about fifteen seconds. Remove it immediately to a large vessel of pure water and wash it until the acid is removed. When the washing is complete, rinse it in a very dilute solution of ammonia, and dry it in the air.

2. *Smokeless Powder*, or *Guncotton*, $C_6H_7(NO_2)_3O_5$.—Guncotton is cellulose in which three atoms of hydrogen have been replaced by three molecules of nitrogen peroxide. It may be prepared by the process outlined in Experiment 74.

EXPERIMENT 74. Mix 3 vols. of pure concentrated sulphuric acid with 1 vol. of nitric acid (specific gravity 1.3), cool the mixture to 10° , and add as much pure cotton, small portions at a time, as will be thoroughly covered by the liquid. Let the preparation stand 24 hrs.

and then remove the cotton and wash it repeatedly in large quantities of clean water. Then let it dry in the air.

282. Properties of Guncotton.—This substance is a white, friable mass which is very unstable. Upon ignition, it burns with such speed that its combustion is practically instantaneous. This is probably due to the fact that it contains a large proportion of nitrogen peroxide, which is a strong oxidizing agent. The speed of combustion is so great, that when the ignition takes place within a confined space, it is attended with a violent explosion. The oxidation is complete, and, since the products are colorless, no smoke is produced. These are the qualities which have caused it to replace black gunpowder to a large extent in warfare.

THE ALBUMENS, OR PROTEIDS

283. Properties of Albumens.—The albumens are organic substances made up of carbon, hydrogen, nitrogen, oxygen, and sulphur. They are amorphous, usually gelatinous substances which do not dissolve readily in water. When heated over the free flame, they decompose into free carbon, ammonia, carbon dioxide, and other gases. The decomposition is attended with the evolution of a peculiar, rather disagreeable odor, like that of burning feathers. The formulas for the albumens have never been determined with accuracy, probably because they have not been obtained in a chemically pure condition. They are widely distributed, in both animal and plant tissues. Many plants which are relatively *poor in starch*, are correspondingly *rich in albumen*. The chief sources of albumen are lean meats cheese, eggs, beans, peas, and lentils. Its abundance in these materials is shown in the following analyses:

TABLE XXXIII*

	WATER	ALBUMEN	FAT	ASH	CARBOHY- DRATE
Beef	76.35	20.54	1.78	1.30	
Veal	78.84	19.86	0.82	0.50	
Mutton.....	75.99	17.11	5.77	1.33	
Herring	74.64	14.55	9.03	1.78	
Eggs	73.67	12.55	12.11	1.12	
Cheese	45.99	30.01	13.41	3.63	5.10
Beans	16.55	26.29	1.51	2.59	44.27
Peas.....	13.40	23.92	1.39	2.75	

The albumens are essential to all animal life. The herbivorous animals draw their supply from the albumen of plants. The human species can use the legumens, peas, beans, lentils, etc., as sources of albumen, but the chief supply is found in eggs, meats, and dairy products.

It will thus be seen that the carbon compounds are the chief sources of our foods. Indeed, the three fundamental classes of foods are fats, carbohydrates, and albumens. The relations of these to our life processes will be more fully discussed later.

EXERCISES

1. Is there any evidence that calcium carbide is an endothermic compound?
2. Why is heat necessary in preparing carbon monoxide from carbon dioxide?
3. Why is sour milk used in preparing "soda" biscuits?
4. Why does distilled water taste flat?
5. What is the chemical difference between vinegar and "hard cider"?
6. Is butter a heat-producing or a muscle-building food?
7. Make a list of the most important starch-producing plants.
8. Would Neave's food (Table XXXI) be suitable for a typhoid fever patient? Imperial Granum? Horlick's?
9. Why is writing paper difficult to burn?
10. Why does guncotton produce no smoke?

* Data from König. This table gives the *average* composition of the different substances.

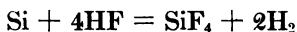
CHAPTER XV

THE CARBON GROUP—(*Continued*)

SILICON, Si (At. Wt. 28.4)

284. Occurrence of Silicon.—This element, first discovered by Berzelius in 1823, is the most abundant in nature, excepting oxygen. It is not found free, but it occurs chiefly in two types of compounds; (1) as quartz, which is the dioxide of silicon, and (2) in combination with oxygen and the common basic elements, such as sodium, calcium, aluminium, etc., in the common silicates, such as clay, the micas, the feldspars, the amphiboles, the pyroxenes, etc., and many other minerals of vast commercial importance. This element, like carbon, shows several allotropic modifications, the amorphous, graphitoidal, and needleshaped crystalline structure.

285. Preparation and Properties of Silicon.—The amorphous variety of silicon may be prepared by igniting an intimate mixture of quartz-sand and magnesium, or by heating quartzite and carbon in the electric furnace. Amorphous silicon is a dark-brown powder which burns to silicon dioxide when heated in the air. It is not acted upon by hydrochloric, nitric, or sulphuric acid, but is dissolved by hydrofluoric acid, with the formation of silicon tetrafluoride and the liberation of hydrogen;



In this reaction silicon acts as a base. Its acid character is shown by its action toward concentrated potassium hydroxide, in which it dissolves, forming potassium silicate;

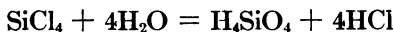


COMPOUNDS OF SILICON

286. Silicon Hydride, SiH_4 , is formed when sand and magnesium powder are melted together in a closed crucible, and the fused mass treated with strong hydrochloric acid. Silicon hydride is a colorless and very combustible gas which burns with a bluish flame, and gives off a white smoke. When it contains a small quantity of free hydrogen, it ignites spontaneously in the air.

287. The Halogen Derivatives.—Silicon forms derivatives with the halogens of the general type, SiR_4 , in which $\text{R} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$. The tetrachloride and tetrafluoride will serve to represent the series.

1. *Silicon Tetrachloride, SiCl_4 ,* is a colorless liquid which boils at 59° , is decomposed by water into silicic acid and hydrochloric acid. The following equation represents the reaction;

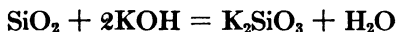


2. *Silicon Tetrafluoride, SiF_4 ,* is a colorless gas with a pungent, penetrating odor. It fumes strongly in moist air, because the moisture decomposes it into silicic acid and hydrofluoric acid, the silicic acid usually separating as a gelatinous mass. This deportment with water shows clearly the negative character of silicon.

288. Oxygen Derivative: Silicon Dioxide, SiO_2 .—Silicon forms but one oxide, SiO_2 , silicon dioxide or silica, which is widely distributed in nature. It crystallizes in two forms, quartz and tridymite, the former being the more common. Quartz is indeed the most abundant mineral in nature. Amethyst, agate, chalcedony, and flint are silicon dioxide colored by a small quantity of some foreign matter, such as iron, manganese, etc. Silica is also found in the stems of many plants, to which it imparts firmness and durability. The cutting power of a blade of corn is due largely to its presence.

Amorphous silica occurs in nature as opal. Various organic secretions of silica are also amorphous.

289. Properties of Silicon Dioxide.—The mineral acids do not affect silica, but it dissolves readily in a boiling solution of sodium or potassium hydroxide, forming the corresponding silicate;



Silica is therefore the anhydride of silicic acid. Being an acid anhydride, it combines with the oxides of many metals at high temperatures to form silicates, some of which are colorless, while others show the most beautiful tints and shades.

290. Silicic Acid. H_2SiO_3 .—This acid has not been isolated, because it decomposes, when heated, into water and silicic acid anhydride. It differs from carbonic acid in that, when its salt is acidified with a mineral acid, the free silicic acid separates as a gelatinous, transparent solid. It presumably has the formula, H_2SiO_3 . It loses water very readily, and is completely dehydrated at a red heat. While carbon shows remarkable power to combine its own atoms into chains, silicon has great ability to hold varying proportions of water. This is, perhaps, its most pronounced chemical characteristic. This deportment gives rise to a series of polysilicic acids. The following table shows their structure and derivation from normal silicic acid, H_4SiO_4 .

TABLE XXXIV



etc.

291. Silicates.—The composition of a silicate depends upon the structure of the acid which it contains. Most of the salts formed under laboratory conditions are derived from H_2SiO_3 . Salts of this type are also found in nature, but most of the natural products are salts of the polysilicic acids. This may be readily seen from the composition of the following minerals:

TABLE XXXV

NAME	FORMULA	ACID
Serpentine . . .	$\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	$\text{H}_6\text{Si}_2\text{O}_7$
Bronzite	MgSiO_3	H_2SiO_3
Diopside	$\begin{matrix} \text{Ca} \\ \text{Mg} \end{matrix} \text{Si}_2\text{O}_6$	$\text{H}_4\text{Si}_2\text{O}_6$
Forsterite	Mg_2SiO_4	H_4SiO_4
Albite	$\begin{matrix} \text{Na}_2 \\ \text{Al} \end{matrix} \text{Si}_6\text{O}_{16}$	$\text{H}_8\text{Si}_6\text{O}_{16}$

292. Uses of Silicon Dioxide and the Silicates.—

Silicon dioxide and the silicates are largely used in the manufacture of glass.

Glass is a solid solution of silicates. There are two chief varieties, the soda-calcium silicates, and the potassium-calcium silicates. The soda-calcium silicate forms a glass which is soft, and fuses at a comparatively low temperature. The potassium-calcium silicate forms a glass, called Bohemian glass, which has a bluish color, and is hard and much less fusible than the soda variety. This latter is much used in chemical work because it is not easily attacked by reagents. Calcium silicate forms a good body for glass, because it crystallizes readily and imparts great rigidity. If the glass were made of this silicate alone, it would be so exceedingly brittle as to break on cooling. This difficulty is overcome by adding sodium or potassium silicate. The two compounds mix uniformly, with the result that the calcium silicate gives firmness

to the glass, while the alkali silicate prevents the calcium silicate from crystallizing. Other forms of glass are merely modified forms of this "mother substance" to suit special purposes. These modifications depend upon the fact that *silicon dioxide possesses anhydride properties*, and is in consequence able to form silicates with the other metallic oxides.

The different varieties of glass may, therefore, be arranged in the following groups: (a) Sodium-calcium-silicate; (b) potassium-calcium-silicate; (c) potassium-lead-silicate; (d) colored glass.

Coloring Glass.—Various and brilliant colors are imparted to glass by dissolving small quantities of certain oxides in the molten mass. These oxides combine with the silicon dioxide, forming the corresponding silicates, which diffuse uniformly through the fused mass, producing beautiful tints. Thus, when one per cent of copper oxide and two per cent of tin are dissolved in molten glass, the cold product is colorless; but when it is again heated to the melting point, it suddenly assumes a deep ruby-red color. This is the process which is used in making the beautiful shades of red which are to be seen in decorated church windows. When the amount of copper reaches about seven per cent of the total weight, the glass becomes so deeply colored that it is opaque.

By varying the coloring oxide, many different colors may be secured. Thus, chromium oxide in small quantity gives a fine green; a little manganese dioxide, a fine violet which becomes black as the quantity of manganese is increased; cobaltous oxide colors potassium glass an inimitable blue, and sodium glass, a fine blue-violet. A white and more or less translucent glass, called enamel glass, is made by adding calcium fluoride (or a mixture of tin and lead) to the ordinary glass body. Gold in a very finely divided state, called Purple of Cassius, gives the most beautiful ruby, crimson, rose, and purple colors. The green color of cheap bottles is due to the

presence of a small quantity of iron which was present as an impurity in the quartz-sand out of which such glass is made.

The process of glass-making consists in heating the mixture of ingredients, sand, sodium carbonate, and calcium carbonate, in conical pots of fire-clay until it is fused into a homogeneous mass. An average charge for sodium glass is:

SiO_2	1450 Lbs.
Na_2CO_3	500 "
CaCO_3	250 "

The state of fusion is maintained until the impurities rise to the surface whence they may be removed as slag. The semi-fluid mass is then worked into the desired shapes. Most small articles are shaped by gravity and air pressure. The method is illustrated in the shaping of a bottle. The operator is provided with a long hollow steel rod, the point of which is plunged into the molten glass and a quantity of the viscous mass is made to adhere to it by rotating it slowly. It is then withdrawn and by swinging it slowly, and simultaneously blowing air into the interior of the mass through the hollow tube, the lump of glass is elongated by gravity, and its transverse diameter is increased by the air pressure, (Fig. 63, A). When the bottle has attained nearly its final form and shape, it is lowered into a mould, Fig. 63, B, and rotated slowly. This gives it a uniform diameter and a smooth surface. Bottles are also made both by a blowing machine, and by pressing the glass into moulds.

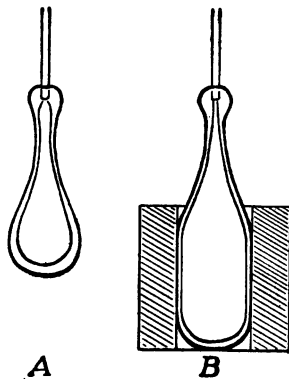


FIGURE 63

Window Glass.—A quantity of glass is blown into a sphere, then elongated into a cylinder by gravity, and its transverse diameter is

simultaneously increased by the air pressure within it. The cylinder is then allowed to cool, and the ends are cut off. It is then cut lengthwise, and placed in a hot-air chamber, where it spreads open into a flat plate, after which it is smoothed by being rubbed with a block of green wood.

Plate glass is essentially window glass which is rolled instead of blown. The molten glass is poured upon an iron table and rolled into large sheets or plates with a hot iron roller. It is then ground smooth and thoroughly polished.

Pressed glass is made in moulds. The molten material is dropped into a die or mould and pressed into it by a metal plunger whose diameter is a little less than that of the mould. Small objects, such as tumblers and pitchers, are made in this way.

Flint glass is a double silicate of potassium and lead which possesses a brilliant luster. It is much used in making lenses for optical instruments, and artificial or "paste" gems.

Cut glass is a flint glass whose design is made by pressing the glass against a rapidly-revolving emery or carborundum wheel. The edges of the cut surface are then polished by rouge (oxide of iron).

"*Granite ironware*" is made of iron covered with an easily fusible glass, called enamel.

Water Glass.—The silicates of sodium and potassium are the only silicates which are soluble in water. The solution, commonly called "water glass," is a thick, syrupy liquid which is extensively used in the manufacture of cements, soaps, artificial stone, and in calico printing.

293. Other Compounds of Silicon.

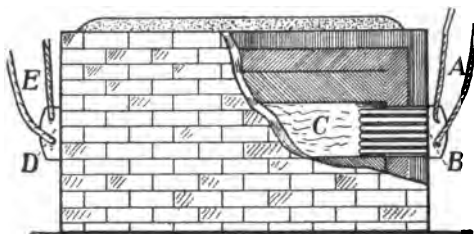


FIGURE 64

1. *Silicon Disulphide*, SiS_2 , is a white amorphous mass which is readily decomposed by water into hydrogen sulphide and silicic acid.

2. *Silicon Carbide*, SiC , has received the commercial name "carborundum." It is produced by heating a

mixture of quartz-sand, coke, and common salt in the electric furnace. Such a furnace is shown in Fig. 64. Its walls are very thick and it is lined with the most refractory kind of fire-clay. The mixture of sand, coke, and salt is placed in the central cavity C, and a very powerful

electric current is passed between the carbon electrodes AB and DE. The resistance with which it meets in passing between the carbon rods creates an intense heat, e.g., 3,500°, and the chemical changes within the furnace are due largely to this high temperature. They may be expressed by the graphs,

1. $\text{SiO}_2 + \text{C}_2 = \text{Si} + 2\text{CO}$
2. $\text{Si} + \text{C} = \text{SiC}$.

Commercial carborundum consists of blue-black crystals which in their hardness rival that of the diamond. Silicon carbide is not attacked by any acid, and dissolves slowly only in fusing potassium or sodium hydroxide. It is much prized as a polishing and cutting material. A wheel coated with this substance, and rotating at a high speed, will cut the hardest steel with comparative ease.

294. The Sub-Group A (Carbon Family).—The similarities and differences in the corresponding derivatives of carbon and silicon may be seen in the following table.

TABLE XXXVI

COMPOUNDS	CARBON	SILICON
The Hydrogen Derivatives	CH_4 ; C_2H_6etc. $\text{CH}_3\text{.OH}$; $\text{C}_2\text{H}_5\text{.OH}$; " H.COOH ; $\text{CH}_3\text{.COOH}$; " $\text{C}_6\text{H}_{12}\text{O}_6$; $\text{C}_6\text{H}_{10}\text{O}_5$; "	SiH_4
1. Physical Properties..	Gas, liquid, or solid.....	Gas
2. Heat of Formation...	$\text{C, H}_4 = 21.8 \text{ Cal}$	$\text{Si, H}_4 = 24.8 \text{ Cal}$.
Halogen Derivatives.....	$\{\text{CCl}_4; \text{C}_2\text{H}_4\text{Cl}_2; \text{etc} \dots$ $\text{CCl}_3\text{.CHO}; \text{etc} \dots\dots$	SiCl_4 ; Si_2Cl_2
1. Physical Properties..	Gases, or liquids chiefly	Liquid
2. Heat of Formation...	$\text{C, Cl}_4 = 21 \text{ Cal}$	$\text{SiCl}_4 = 157 \text{ Cal}$.
3. Boiling Point.....	$\text{CCl}_4 = 76.7^\circ$	$\text{SiCl}_4 = 59^\circ$
Oxygen Derivatives.....	CO ; CO_2	SiO_2
1. Physical Properties..	Gases.....	Solid
2. Heat of Formation...	$\text{C, O}_2 = 97 \text{ Cal}$	$\text{Si, O}_2 = 219 \text{ Cal}$.
Sulphur Derivatives.....	CS_2	Si, S_2
1. Physical Properties..	Liquid.....	Solid
2. Heat of Formation...	$\text{C, S}_2 = -26.1 \text{ Cal}$	$\text{Si, S}_2 = 40.4 \text{ Cal}$.
3. Boiling Point.....	47°	Sublimes

EXERCISES

1. To what commercial use is pure quartz put?
2. Would mica boxes be serviceable for storing potassium fluoride?
3. Would glass vessels be suitable for making soft soap?
4. Why are some pieces of glass so much more brittle than others?
5. What would be the properties of a glass which contained only a silicate of sodium or potassium?
6. Of what use is sodium silicate in soap-making?
7. Will its presence improve the soap?
8. With what could a broken dish be cemented so that it would not be changed by boiling water?
9. How many pounds of sodium carbonate must be added to 800 lbs. of pure sand to form pure sodium silicate?
10. What are the physical properties of a glass which contains 5 per cent of copper?

CHAPTER XVI

THE CARBON GROUP—(*Continued*)

SUB-GROUP B; LEAD AND TIN

There are many points of similarity between these two elements and between their corresponding derivatives. They possess the fundamental attributes of metals (metallic luster, fusibility, etc.), and their oxides are primarily basic in character. It is to be observed, however, that several of their oxides act as anhydrides when they are associated with the hydroxides of sodium and potassium. Lead is the more basic, for its hydroxide has feeble alkaline properties. With strong acids, both elements form neutral salts which show a tendency to decompose and form basic salts. This deportment indicates the relation of the two elements to carbon and silicon.

LEAD, Pb (AT. WT. 206.9)

295. Occurrence and Preparation of Lead.—This element, which was known to the Ancients, is not found free, but its compounds are abundant. Chief among them is galena, PbS , from which most of the commercial supply of lead is obtained. Its metallurgy is comparatively simple. The powdered ore is first

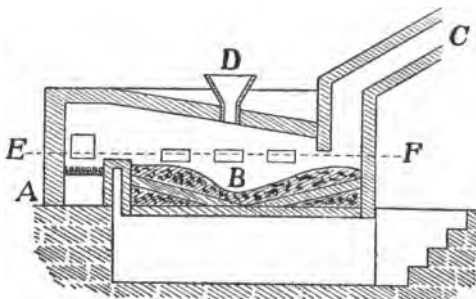
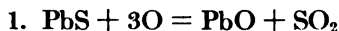


FIGURE 65

roasted in a reverberatory furnace, Fig. 65, the temperature of which is kept below the melting point of lead. Much of

the sulphide is thus oxidized to lead oxide and lead sulphate, but a portion of the lead sulphide remains unchanged;



The mixture is then melted in the absence of air. The following reductions take place:



Another method, called the "carbon process," is well adapted to the metallurgy of some ores. In this process the ore is roasted at a comparatively low temperature in a current of air, which converts the major portion of the lead sulphide into lead oxide. The oxide is then reduced with coal or coke.

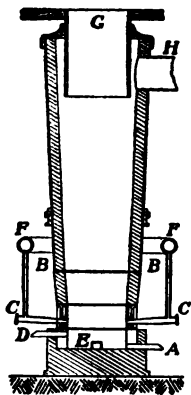


FIGURE 66

The reduction is effected in furnaces similar in construction to the blast furnace used for reducing iron oxide. Such a furnace is shown in Fig. 66. The central shaft is fed with the roasted ore and coal from the cylinder G. The fire in the crucible is maintained by the air blast from the pipes C C, which are connected with the main air-pipe F F. The reduced and molten lead collects at the bottom of the crucible, and the slag which floats upon its surface is removed at D. The molten lead is then drawn off at A.

296. Properties of Lead.—Lead is a bluish-gray metal, notable for its malleability and softness. It is not tenacious and cannot, therefore, be drawn into wire. It is not acted upon by dry air, but is quickly coated with a thin film of the oxide or basic carbonate when exposed to air and moisture. This film protects it from further change. Lead is so soft that it may be scratched with the finger-nail, and when drawn across

a sheet of paper leaves a blue-black mark. Sulphuric or hydrochloric acid has but little effect upon it, but nitric acid dissolves it readily, forming lead nitrate.

297. Uses of Lead.—Lead is extensively used for the manufacture of lead pipes and sheet lead for roofs, sinks, etc. The large chambers used in the manufacture of sulphuric acid are lined with it. The resistance of lead pipes to the action of the air and moisture has brought about their general use for carrying water for drinking purposes. It is noteworthy, however, that water which contains carbonic acid anhydride, organic matter, soluble nitrates, soluble chlorides, or ammonia, exercises a solvent action upon the lead. Some of it passes into solution and, as all soluble lead salts are poisonous, such water becomes very unwholesome. Lead is also widely used in the manufacture of alloys. Chief among these are:

TABLE XXXVII*

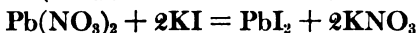
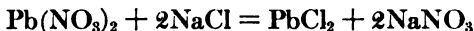
	LEAD	ANTIMONY	TIN	ARSENIC
	Parts	Parts	Parts	Parts
Type-metal.....	4	1		
Shot-metal.....	110			1
Shot-metal.....	100			.8
Soft-solder.....	10		1	
Pewter.....	1		4	

COMPOUNDS OF LEAD

298. Halogen Derivatives.—The general type of these compounds is PbR_2 ($\text{R} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$), since derivatives of the type PbR_4 (except PbCl_4) have not been obtained. The dichloride, PbCl_2 , and the iodide, PbI_2 , which are the most important, may be prepared by precipitation from a solution

*Data from Hiorns. Other proportions of the metals are also used.

of lead nitrate with the corresponding halogen acid or its soluble salt:



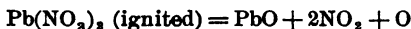
a. *Lead Chloride* is a white, crystalline powder which dissolves sparingly in cold water.

b. *Lead Iodide* is a lemon-yellow salt, practically insoluble in water, and is used to some extent in medicine.

299. Oxygen Derivatives.—There are five oxides of lead;

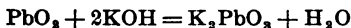


1. *Lead Monoxide*, PbO , the most important, is easily prepared by heating lead nitrate to dull redness;

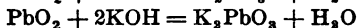
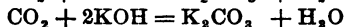
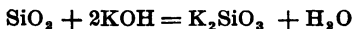


It is a yellow, amorphous powder, which dissolves very sparingly in water, forming an exceedingly weak alkaline solution. It is primarily basic, although it sometimes shows anhydride properties. This double capacity is shown in its deportment toward acetic acid, and sodium hydroxide. Acetic acid dissolves it easily, forming lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Sodium hydroxide, in considerable excess, forms sodium plumbite, Na_2PbO_2 . Such deportment indicates a metalloidal character for lead.

2. *Lead Dioxide*, PbO_2 , a red-brown powder which may be prepared by fusing together 4 parts of lead oxide, PbO , 8 parts of potassium nitrate, and 1 part of potassium chlorate, is a strong oxidizing agent. Its acid properties are more pronounced than those of the monoxide. It dissolves in concentrated hot potassium hydroxide, forming potassium plumbate;



Its relation to silicon dioxide and carbon dioxide is seen in the following potassium salts:



3. *Red Lead, Minium*, Pb_3O_4 , is formed when lead monoxide is heated to about 400° in the air. The commercial minium varies in color from red to yellow. It is decomposed at a high temperature into lead monoxide and oxygen. Nitric acid decomposes it, forming

soluble lead nitrate and insoluble lead dioxide, which indicates that it is a mixed oxide containing two molecules of the monoxide and one molecule of the dioxide. Red lead is used as a pigment in making red paint for iron work, as a flux in the manufacture of porcelain, as a cement in plumbing and gas-fitting, and as a substitute for lead monoxide in the manufacture of flint glass.

300. Salts of Lead.—The most important salts of lead are the nitrate, sulphate, chromate, and carbonate.

I. *Lead Nitrate*, $\text{Pb}(\text{NO}_3)_2$, is easily prepared by dissolving metallic lead, lead oxide, or lead carbonate in nitric acid, and crystallizing the product (p. 9).

II. *Lead Sulphate*, PbSO_4 , is always formed when sulphuric acid or a soluble sulphate is added to a solution of a lead salt. It is a heavy white solid which is practically insoluble in water but dissolves sparingly in the strong mineral acids. It is in part decomposed by fusion into lead monoxide and sulphur trioxide.

III. *Lead Chromate*, PbCrO_4 , will be discussed later.

IV. *Lead Carbonate*, PbCO_3 , is a white amorphous salt, produced when solutions of lead nitrate and ammonium carbonate are mixed. When a solution of sodium carbonate is used, a basic carbonate is formed, the structure of which is not constant. It usually has the composition, $\text{PbO} \cdot 2\text{PbCO}_3 + \text{H}_2\text{O}$. This compound, known commercially as "white-lead," is used extensively in the manufacture of white paint. The value of lead paint is due to its durability and covering power, a very thin layer producing a perfectly smooth white surface.

301. Paints and Painting.—Protective painting consists in covering a surface with an adhesive mixture which hardens spontaneously and thus protects it from the air and moisture. The "body" of ordinary house paint is usually made of finely ground white-lead, to which sufficient linseed oil is added to give to it the consistency of a very thin paste. Such a mixture gives a uniform coating, but it sets or dries slowly. The drying is hastened by adding a small proportion of benzine, turpentine, boiled linseed oil, litharge, or sugar of lead ground in oil. The benzine and turpentine promote the drying because they evaporate readily, but the boiled oil and

litharge, or sugar of lead, increase the speed with which oxygen is absorbed by the oil.

A white paint of excellent quality is made of zinc oxide and linseed oil. It resists the action of hydrogen sulphide and other volatile sulphur compounds, but it has less body than lead paint. Its preparation requires considerable care, because any excess of oil forms a gummy surface which hardens very slowly. A very good paint, which is especially adapted for inside work, is made of white lead and zinc oxide ground in boiled linseed oil, to which a drying agent has been added. This paint hardens readily and gives a beautifully white, glossy, and durable surface.

Much of the white-lead which is marketed contains a large percentage of barium carbonate or sulphate. Both of these salts are heavy and white, so that their presence is not easily detected; but a paint which is prepared from such a mixture does not harden to a compact mass. It forms a dry and more or less chalky surface, which will not resist the action of the air and moisture.

Ready-mixed paints usually contain a high percentage of finely ground calcium carbonate mixed with the lead carbonate. Such a paint covers fairly well, but it is not durable.

Colored paints are made by grinding the body of the paint (e.g., lead carbonate) with a mineral coloring compound, such as red and yellow ochers, vermilion and Venetian red, Prussian blue, chrome yellow, etc.

Woods are also protected by filling the pores with a hardening mixture and then coating the surface with varnish. This kind of finishing preserves the natural grain of the wood and gives a smooth, glossy surface.

The hardening mixture or "filler" is made of boiled linseed oil and flour, cornstarch, whiting (powdered CaC_2), etc. The flour or other body is mixed with the oil until it forms a thick paste. This is applied to the surface with a brush, and allowed to stand until it "sets" or hardens to a stiff coating. The surplus material is then rubbed off, and the varnish is applied.

Varnish is made of a drying oil which contains resin in solution. The resins in general use are rosin, mastic, amber,

copal, dammar, or shellac. For some varnishes, the drying oil is the solvent, while other resins require benzine, turpentine, alcohol, etc., for their solution. Hence a varnish may be classified according to its solvent. There are three chief classes in daily use: (1) spirit, (2) turpentine, and (3) oil varnishes.

I. Spirit varnishes are usually made of shellac dissolved in wood alcohol. They give a coating which has a fine gloss, but it cracks readily. They also act as a filler and are much used to harden wood before an oil varnish is applied.

II. Turpentine varnishes are usually made of dammar resin dissolved in turpentine. To increase the tenacity of this varnish and avoid cracking, boiled linseed oil is usually added.

III. The oil varnishes are made by dissolving copal or some other resin in linseed oil, and adding a sufficient quantity of turpentine. Coach varnish No. 1, which is so extensively used in finishing vehicles and other hard woods, belongs to this class of varnishes. It is made from Kauri gum, a very valuable material mined in New Zealand, and which is the fossil exudation from a gum-producing tree which is now extinct. Coach varnish dries slowly, but the coat is hard, elastic, and does not scratch. Varnish which is made from ordinary rosin dries rather quickly, but the coating scratches easily, and is readily discolored by water, alcohol, etc.

The manufacture of oil varnishes is difficult, because the hard and semi-hard resins dissolve in oil only when it is boiling, and the resin is heated to 230° – 360° . Hence the resin is melted in a metal pot, C, Fig. 67, and the boiling linseed oil is added to the fluid mass. The mixture

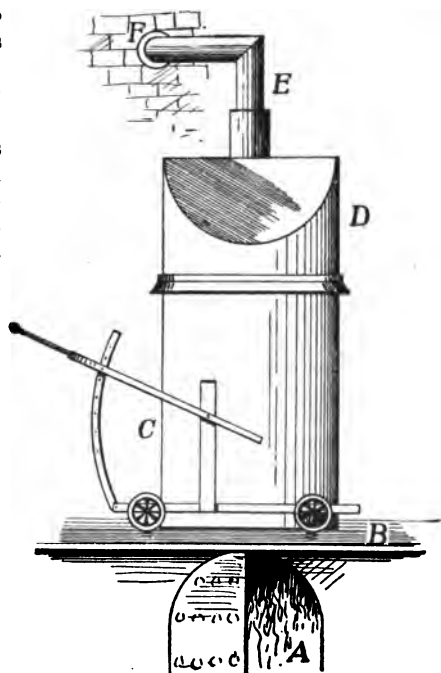


FIGURE 67

is then boiled until it becomes perfectly clear, after which it is allowed to cool and is thinned with turpentine.

The linseed oil which is used in preparing paints and varnishes is obtained from the seed of the common flax. It contains a compound of linoleic acid, $C_{18}H_{34}O_2$, which, on exposure to the air, absorbs oxygen and forms oxylinoleic acid, $C_{18}H_{32}O_5$. This substance possesses the properties of a resin.

TIN, SN (AT. WT. 119)

302. Occurrence and Preparation of Tin.—Tin is not found free, and its compounds are few and sparingly distributed. Tin-stone, cassiterite, is the ore from which practically all of the commercial tin is obtained. It is found in England, Germany, Australia, the East Indies, and to some extent (though not in commercial quantity) in the Black Hills of South Dakota. When it is taken from the vein, it contains other minerals, such as galena, iron pyrites, copper pyrites, arsenical ores, etc. The tin-stone usually forms only about 5 per cent of the whole.

It is freed from its impurities as much as possible by crushing and washing the ore. The light earthy materials are thus removed and the tin-stone remains, mixed with other heavy minerals. The residue is roasted, ground, and washed a second time, and the second residue, called "black tin," is then smelted. In this process, the "black tin" is mixed with about one-fifth of its weight of hard coal and the mixture is thrown upon the hearth of a reverberatory furnace (Fig. 65) and heated for about six hours. The reduced tin is then drawn off into pots, or moulded into blocks. These blocks are further purified by being heated on the sloping hearth of the furnace to the melting point of the tin, 231° . The tin then runs off, and is collected in a pot, while the unmelted impurities remain. The tin in the pot is then poled. This consists in plunging a pole of green wood below the surface of the molten tin. Any impurities which come to the surface are skimmed off and the tin is moulded into blocks.

303. Properties of Tin.—Tin possesses a brilliant white luster. Its attributes vary with the temperature. At 100° it is

ductile and malleable, but at 200° it is so brittle that it may be reduced to a fine powder. When it is heated to a white heat in the presence of air, it ignites and burns with a pale blue flame. It dissolves in hot concentrated hydrochloric acid, forming stannous chloride; but concentrated nitric acid changes it to insoluble metastannic acid, H_2SnO_3 . These two reactions show its metallic and non-metallic character.

304. Uses of Tin.—Tin is extensively used in the manufacture of solder and other alloys, and in the making of tin-plate. To make tin-plate, sheet iron is carefully cleansed, dipped into vats of molten tin, and drained. This forms the sheet tin from which cans, cooking vessels, etc., are made. Tin vessels are adapted to the preservation of acid fruits, because tin is not corroded appreciably by weak acids.

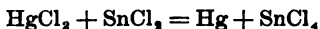
COMPOUNDS OF TIN

Tin forms two series of compounds, the stannous and stannic.

305. Halogen Derivatives.—There are two types of these derivatives, SnR_2 , and SnR_4 .

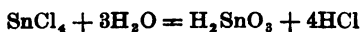
The chlorine derivatives are the most important, because they are useful in the arts.

1. *Stannous Chloride*, SnCl_2 , is formed when concentrated hydrochloric acid acts upon tin. It is a white, crystalline mass which melts at 250° , and distills at 606° . It possesses strong reducing properties. It reduces mercuric chloride to metallic mercury, and compounds of arsenic, to metallic arsenic;



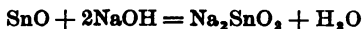
This seems to indicate that the normal combining valence of tin is four.

2. *Stannic Chloride*, SnCl_4 , formed by oxidizing stannous chloride, is a fuming liquid which combines with a little water to form a crystalline mass. Boiling water decomposes it into stannic acid and hydrochloric acid;



306. Oxygen Derivatives.—Tin forms two oxides, SnO and SnO_2 .

1. *Stannous Oxide*, SnO , is a brown-black powder which takes up oxygen and forms SnO_2 . It possesses weak basic properties in that it combines with strong acids to form salts which are not very stable. It shows acid anhydride properties by dissolving in concentrated sodium hydroxide;



Sodium stannite, Na_2SnO_2 , is a strong reducing agent.

2. *Stannic Oxide*, SnO_2 , is a white amorphous powder whose chemical properties are similar to those of the monoxide in that it possesses both basic and acid properties. As a base, it forms stannic salts, such as SnCl_4 ; as an acid, it forms stannates, such as Na_2SnO_3 . Both the stannic salts and the stannates are used extensively as mordants in dyeing and calico printing, because they develop brilliant colors.

307. The Sub-Group B (Carbon Family).—The following table gives a general view of the attributes of lead and tin, and their corresponding derivatives.

TABLE XXXVIII

	TIN	LEAD
Atomic Weight .	119	206.9
Specific Gravity .	7.29	11.37
Melting Point. . .	231°	327.7°
Chlorides	SnCl_2 ; SnCl_4	PbCl_2 ; PbCl_4
Oxides	SnO ; SnO_2	PbO ; Pb_2O_3 ; PbO_2 ; etc.
Sulphides	SnS ; SnS_2	Pb_2S ; PbS
Hydroxides	$\text{Sn}(\text{OH})_2$; $\text{Sn}(\text{OH})_4$.	$\text{Pb}(\text{OH})_2$
Carbonates		PbCO_3

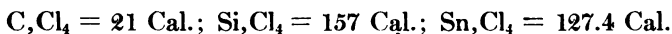
THE CARBON FAMILY

308. It has already been pointed out that carbon and silicon are much alike in their fundamental attributes. Their dioxides are acid anhydrides and the attributes of the other

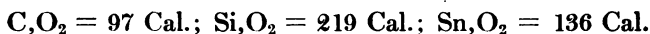
derivatives all point to the non-metallic character of the two elements. Tin and lead are metals whose oxides possess acid and basic properties, and whose other derivatives are much alike. Notwithstanding these patent differences between the two groups, there are the following points of resemblance upon which their grouping into a natural family is based.

1. The physical attributes of the four elements *vary with increase* in the atomic weight.

2. Their affinity for the halogens seems to increase with increase in the atomic weight. This is shown by the increasing heat of formation, if that be taken as a measure of affinity;



3. The same heat relation is relatively true of the oxides;



4. The basic properties increase with increasing atomic weight. This is shown by the attributes of the hydrogen, halogen, and oxygen derivatives.

a. Carbon and silicon form hydrides; lead and tin do not.

b. The halogen derivatives of carbon and silicon show a tendency to form acids when they are dissolved in water. The corresponding compounds of tin decompose very slowly in water, while the like compounds of lead are comparatively stable.

c. The dioxides of carbon and silicon are normally acid anhydrides. The dioxide of tin acts as a base and an acid anhydride, while the dioxide of lead, though an anhydride when associated with sodium hydroxide, readily breaks up into oxygen and basic lead monoxide.

It will be observed that the similarities in the attributes of these four elements and their corresponding derivatives are not so striking as those in the preceding groups. They are, however, considered to be sufficient to cause the four elements to

be grouped together in a natural family. The following table will make these relations more apparent.

TABLE XXXIX

	CARBON	SILICON	TIN	LEAD
Atomic Weight.	12	28.4	119	206.9
Specific Gravity	2.2 (graphite)	2.49	7.29	11.37
Melting Point..			231°	327.7°
Chlorides.....	CCl ₄ ; etc....	SiCl ₄ ...	SnCl ₄ ; SnCl ₂	PbCl ₂ ; PbCl ₄
Oxides.....	CO; CO ₂	SiO ₂ ...	SnO; SnO ₂ ..	PbO; PbO ₂ ; etc.
Sulphides.....	CS ₂	SiS ₂ ...	SnS; SnS ₂ ..	Pb ₂ S; PbS
Hydrides.....	CH ₄ ; etc....	SiH ₄ ...		

EXERCISES

1. What are the chemical properties of silicon dioxide which adapt it to glass-making?
2. Would it be adapted to such use, if it were an endothermic compound? A basic oxide?
3. Why is silicon dioxide more suitable than carbon dioxide for making glass?
4. Why are pewter vessels not suitable for cooking?
5. Would a paint made of white-lead and lubricating oil (p. 264) dry readily?
6. Will a strong solution of sodium carbonate remove varnish from old furniture? Turpentine?
7. Explain the fact that an emulsion of chloroform, ammonia, and sweet oil will remove scratches from varnished surfaces.
8. Would it be good economy to make soap in tin kettles? Why?
9. Why is a small piece of tin placed on the top of the meat in a can of salmon?
10. Why is lead put into tinner's solder?

CHAPTER XVII

THE BORON GROUP OF ELEMENTS: GROUP V.

309. Properties of Groups I, II and III.—It was pointed out in the introduction to Chapter XIV that the mutual relations of the halogen, the oxygen, and the nitrogen families of elements are to be found in the lessening affinity for hydrogen with increase in atomic weight, and the general increase from the halogen to the nitrogen group in the basic properties of the corresponding compounds. Thus, if each column of compounds in Table XIX, page 244, be read from the top downward, it will be noted that the lowest compound is more basic or less acid in its properties than the corresponding compound in the top column. It will be valuable to place the members of the carbon group into juxtaposition with these three groups (p. 314) and observe whether or not this general trend of the compounds toward the basic condition will continue.

Only two of the elements in the carbon group form hydrogen derivatives, and these derivatives are neutral compounds. The fact that tin and lead do not form such derivatives indicates their basic character. The oxygen derivatives of the carbon group show that this group is *more* basic than the preceding groups. Thus, all of the dioxides are acid anhydrides, but they form much weaker acids than the oxygen derivatives of the nitrogen group. For instance, carbonic acid anhydride and silicic acid anhydride are so weak that they can be displaced from their compounds by comparatively weak acids, such as acetic acid, and the oxides of tin and lead are anhydrides

only when associated with strong bases like sodium hydroxide. It will be noted also that the basic properties of the carbon family *increase* from carbon to lead. Collectively this group may be said to be more basic than any of the preceding groups. It will be noticed in Table XL that there is no

TABLE XL

	Element	Derivative	Heat of Formation	Reaction	Element	Derivative	Heat of Formation	Reaction
I. The Halogen Group...	F	HF	37	A	Cl	HCl	23	A
II. The Oxygen Group....	O	H ₂ O	57	N	S	H ₂ S	4.5	WA
III. The Nitrogen Group...	N	H ₃ N	11.8	Alk	P	H ₃ P	11.6	WB
IV. The Carbon Group.....	C	H ₄ C	21.8	N	Si	H ₄ Si	24.8	N

	Element	Derivative	Heat of Formation	Reaction	Element	Derivative	Heat of Formation	Reaction	Element	Derivative	Heat of Formation	Reaction
I...	Br	HBr	8.4	A	I	HI	-6.4	A				
II..	Se	H ₂ Se	-5.4	WA	Te	H ₂ Te	-19.4	WA				
III..	As	H ₃ As	-11.7	N	Sb	H ₃ Sb	-84.5	N	Bi			
IV ..					Sn				Pb			

A = Acid. WA = Weak Acid. N = Neutral. WB = Weak Base.

element in the carbon group which corresponds to arsenic of the nitrogen group. Such an element, Germanium, is known, but it is so rare that reference to it was omitted. The next group of elements, which stands in close relation to the carbon group, is the boron-aluminium family.

310. General Properties.—This group includes a number of elements, only two of which are found abundantly

and possess commercial importance. These are boron and aluminium. They are placed in the same group because of their atomic weight relations, and the similarity in the *structure* of their corresponding derivatives. The physical and chemical properties of the elements and of their corresponding derivatives are very dissimilar. Boron is an amorphous powder which does not possess any of the characteristic attributes of a metal; aluminium is a hard and more or less crystalline mass, all of whose attributes are metallic. The chemical properties of their derivatives are equally unlike. Boron forms a hydrogen derivative, H_3B ; its oxide is an acid anhydride which resembles silicon dioxide in its power to form poly-acids, and its halogen derivatives show the same instability as the corresponding derivatives of silicon. Aluminium does not form a hydrogen derivative, which denotes a departure from the true non-metallic character. Its oxide is primarily basic in character, although it possesses feeble anhydride properties when associated with strong bases, and its halogen derivatives are much more stable than those of boron.

BORON, B (AT. WT. 11)

311. Occurrence of Boron.—This element, first prepared in a pure form in 1807 by Davy, is not found free, but occurs chiefly in combination with oxygen as boric acid, H_3BO_3 , and in borates. Boric acid is found in the steam which issues from the earth in certain volcanic regions, particularly in Tuscany. The steam is conducted into artificial or natural pools, the water of which soon becomes charged with the acid in solution. This liquid is then evaporated to dryness and the acid is recovered. Its most important salt is sodium tetraborate, $Na_2B_4O_7$, commercially called "borax."

312. Properties of Boron.—It is a soft, chocolate-brown powder which dissolves sparingly in water. When heated in

the air it burns easily, forming boric oxide, B_2O_3 , and a small quantity of boron nitride, BN. Liquid oxidizing agents, such as nitric acid, aqua regia, and fusing nitrates, change boric oxide into boric acid, H_3BO_3 .

COMPOUNDS OF BORON

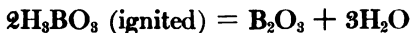
313. Hydrogen Derivatives.—Boron hydride, BH_3 , may be prepared by fusing a mixture of boric acid and magnesium powder and treating the resulting mass with dilute hydrochloric acid. The boron hydride is a colorless gas which burns with an intensely green flame. When a cold dish is depressed into the flame, the boron is deposited upon it as a brown-black mass. In this respect BH_3 is similar to arsenetted hydrogen (p. 234).

314. Halogen Derivatives.—Boron combines directly with fluorine, chlorine, and bromine to form the corresponding derivatives. The chloride, BCl_3 , is a colorless liquid which boils at 18° . It is readily decomposed by water into boric acid and hydrochloric acid;



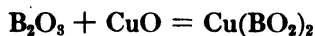
In this respect it resembles silicon tetrachloride (p. 293).

315. Oxygen Derivative.—Boron forms one oxide, B_2O_3 , a colorless, glass-like substance which is formed when boric acid is melted;



It combines directly with the oxides of most metals, forming the corresponding borates. B_2O_3 is, therefore, an acid anhydride. This may be illustrated by heating a little boric acid or borax in the loop of a platinum wire until it fuses to a colorless, glass-like bead, dipping the bead, while hot, into some copper oxide, and exposing the bead and copper oxide to a strong

oxidizing flame from the blow-pipe. A fine blue-green bead will be formed. The reaction may probably be expressed by the equation,



316. Boric Acid, H_3BO_3 , crystallizes in colorless, shining plates which feel greasy to the touch. It is a tribasic acid, forming salts, the borates, with metallic bases. When the free acid is heated, it acts much like silicic acid; that is, it loses water in varying proportions and forms polyboric acids.

Boric acid is used in medicine to disinfect wounds and to allay inflammation, and in the arts to preserve foodstuffs.

317. The Borates.—The salts which boric acid forms with bases possess a varied and complicated composition from the fact that the acid may lose one or more molecules of water when it enters into combination. The result is the formation of metaborates or tetraborates. Borax, $\text{Na}_2\text{B}_4\text{O}_7$, the most important compound of boron, is found in large deposits in Nevada and California. It is useful as a cleansing agent and disinfectant. Large quantities are used in laundries. It is also used for preserving meats and other canned goods. Fusing borax dissolves the oxides of metals with facility (p. 316). This property makes it an admirable agent for cleansing metallic surfaces that are to be soldered or welded. It is also used in the manufacture of enamels and glazes for pottery and porcelain, and it even finds a limited use in medicinal preparations which are designed to relieve inflammation, as in tonsillitis, eczema, and conjunctivitis.

ALUMINIUM. (At. Wt. 27.1)

318. Occurrence of Aluminium.—Aluminium is the third most abundant element, making up rather more than 8 per cent by weight of the earth's crust. It does not occur free,

but is found in the form of oxides and silicates. Its silicates are numerous, and are abundantly and widely distributed. They are the essential constituents of many rocks, and the disintegration-products of these rocks make up the principal body of our soils. Among the most important of the silicates are the feldspars, the micas, and the amphiboles. Some of the compounds of aluminium which are of great importance to-day were formed by the weathering of these silicates. Thus clay which is so widely distributed is a product of weathering, and kaolin, the most valuable form of clay, is an aluminium salt of orthosilicic acid, H_4SiO_4 .

319. Preparation of Aluminium by Electrolysis.—At present it is prepared on a large scale by various electrolytic processes, of which the following is perhaps the most used:

Hall's Process.—The apparatus used consists essentially of an iron box B (Fig. 68)*, which is lined with powdered coke that has been

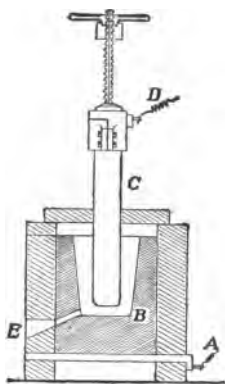


FIGURE 68

cemented into a compact mass by tar, sugar, or some other organic carbon compound. The bottom of the box acts as the — electrode and it is connected with a dynamo by the copper wire A. The + electrode is made of a heavy carbon rod, C, which is also connected with the dynamo by a heavy copper wire D.

A mixture which consists of about 31 parts of aluminium fluoride and 40 parts of powdered cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$, is placed in the box, and the carbon rod C is lowered nearly to the bottom of it. The cryolite mixture is then fused, either by heating the box directly or by passing a strong electric current. If the current is used, the resistance which it meets in passing through the cryolite to the bottom of the box generates sufficient heat to melt the cryolite, and to maintain it in a liquid state. Pure dry aluminium oxide is then added to the fused cryolite, in which it dissolves readily. A current with an electromotive force of approximately six volts is passed through the fused mass. The oxide is separated into its ele-

* Figure 68 is from Borches & McMillan's *Electric Smelting and Refining*.

ments; the aluminium collects on the bottom of the box and is drawn off from time to time through the tap E; the oxygen migrates to the positive electrode C, where it combines with some of the carbon to form carbon monoxide, which escapes.

The cryolite mixture is especially adapted to the process, since it is a ready solvent for the aluminium oxide, and is not itself decomposed by the strength of current which is usually employed. The process therefore is continuous, and the initial charge of cryolite and aluminium or calcium fluoride may be used for a long period. It is only necessary to replenish from time to time the aluminium oxide which has been reduced. One company which draws its power from Niagara Falls produces annually from four to five thousand tons of aluminium by the Hall process.

320. Properties of Aluminium.—Aluminium is a ductile and malleable metal which has about the color of tin. It is very light, its specific gravity being only 2.56. Because of its ductility and malleability, it is adapted to the manufacture of wire and plate wares. It is not altered in the air either by a gentle heat or moisture. Its lightness and rigidity also make it a very desirable material for the manufacture of scale beams, dial plates, and other parts of delicate physical and chemical apparatus. It is not altered by cold nitric or sulphuric acid, but it dissolves with ease in hydrochloric acid, or the hydroxides of potassium and sodium, with the evolution of hydrogen. The very great abundance and wide distribution of its compounds, and the admirable properties of the metal make aluminium an object of great importance to the commercial and scientific world. As yet it has not found a wide application in the industries, because it costs too much to extract it from its combinations.

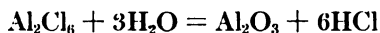
321. Uses of Aluminium.—Aluminium is used in making steel, copper, and brass castings. It has been found that when a small quantity of it is added before casting these metals, it produces a very uniform cast which is largely free from air cavities. It also finds some use in the preparation of

alloys. An aluminium bronze, which is an alloy of copper and aluminium (9:1), is strikingly similar to gold. It is prepared by melting copper, aluminium oxide, and carbon in the electric furnace.

COMPOUNDS OF ALUMINIUM

322. Halogen Derivatives.—Aluminium combines directly with the halogens, forming compounds of the general type, Al_2R_6 ($\text{R} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$). The chloride is the most important of these derivatives.

Aluminium Chloride, Al_2Cl_6 , is a white, crystalline mass which melts at 193° . It dissolves in water to a clear fluid, but when the solution is evaporated to dryness and ignited, the salt is decomposed into its oxide and hydrochloric acid;

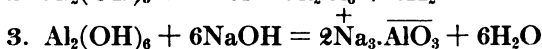
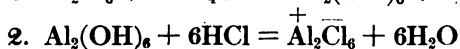
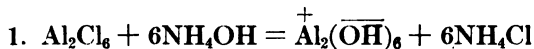


This shows that aluminium possesses rather feeble basic properties.

323. Oxygen Derivative.—Aluminium forms but one oxide, Al_2O_3 , which occurs in nature in the mineral corundum. It forms very hard, hexagonal crystals, which are sometimes colored with small quantities of other oxides. Thus, a little chromium gives it a fine red color, forming the ruby; cobalt yields the blue sapphire, the yellow "oriental topaz," and the violet "oriental amethyst." "Emery" is an impure compound of corundum and iron oxide. It is very hard, and serves as an abrasive and polishing material for glass, steel, and other hard materials.

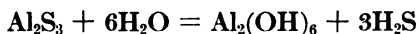
324. Aluminium Hydroxide, $\text{Al}_2(\text{OH})_6$, is formed by making the solution of its chloride or sulphate slightly alkaline with ammonia. It is a gelatinous and more or less transparent solid which is insoluble in water, but dissolves in the strong

acids or the caustic alkalis. This shows the dual character of aluminium. The chemical changes may be expressed by the graphs,



In the first and second equations, aluminium shows only basic properties, while in the third it is acid in character. The hydroxide may, therefore, be viewed as a weak acid, and the oxide as a weak acid anhydride.

325. Other Compounds of Aluminium.—Aluminium is more basic than acid in its fundamental properties, but it is so feeble a base that it cannot form stable salts with such weak acids as carbonic, sulphurous, hydrosulphuric, etc. Thus, when a solution of aluminium chloride is precipitated with ammonium sulphide, presumably aluminium sulphide, Al_2S_3 , is at first formed, but it decomposes at once into aluminium hydroxide and hydrogen sulphide;



326. Salts of Aluminium.—Aluminium forms many salts, in most of which it acts as a positive element. These salts are both simple and double. Of the simple salts, the sulphate, $\text{Al}_2(\text{SO}_4)_3$, is probably the most important. It forms porcelain-like scales which dissolve readily in water, producing a perfectly colorless liquid. It is used extensively for the manufacture of alums, and as a mordant.

327. Alums.—The alums are the best representatives of the double salts of aluminium. Potash alum, the most com-

mon of these, is prepared by mixing equi-molecular quantities of aluminium sulphate and potassium sulphate, and crystallizing the product. Potash alum may be prepared as outlined in Experiment 75.

EXPERIMENT 75. Dissolve 10 gm. of aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and 2.6 gm. of potassium sulphate, K_2SO_4 , in 200 cc. of distilled water, concentrate the solution to about half its volume, place the liquid in a small beaker, and allow it to stand until crystals separate from the solution.

Potash alum, or "alum" ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$), forms beautiful octahedral crystals which dissolve readily in water, forming a slightly acid, astringent-tasting solution. It is used extensively as a mordant (p. 333) in dyeing and printing cloth, in the manufacture of leather and paper, for hardening plaster in fresco-painting, in medicine, and for making combustible materials fire-proof. Other alums may be prepared in like manner by substituting the sulphate of any other alkali metal for the potassium sulphate. Hence there exist:

$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, potassium alum

$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, sodium alum

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, ammonium alum

Alums may also be formed by substituting for the aluminium sulphate the sulphate of iron, manganese, or chromium.

$\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, ferric alum

$\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, chromium alum

$\text{K}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, manganese alum

These alums all crystallize in the same forms, and they all possess the same fundamental chemical attributes.

328. The Silicates of Aluminium.—These salts are to the inorganic world what the derivatives of carbon are to the organic. The most important of them, commercially, are the feldspars, of which orthoclase, $\text{K}_2\text{AlSi}_6\text{O}_{16}$, and albite (or soda

feldspar), $\text{Na}_2\text{AlSi}_6\text{O}_{16}$, are among the most widely distributed and abundant. The feldspars, especially orthoclase, quartz, and mica, the last itself a complex aluminium silicate, are the essential minerals of granite.

329. Kaolin.—The disintegration of feldspar by weathering gave rise to kaolin, which, in its purest form, is an aluminium silicate. Its composition varies. Some specimens yield the formula, $\text{Al}_4(\text{SiO}_4)_3 \cdot 4\text{H}_2\text{O}$; others have the structure $\text{H}_4\text{AlSi}_2\text{O}_9$. On the decomposition of the feldspars, potassium and sodium silicates were probably formed, dissolved in water, and carried off by streams, while the insoluble silicate of aluminium, together with the hydroxides of iron remained. The following table contains the analyses of four samples of kaolin.

TABLE XLI*

INGREDIENTS	No. 1	No. 2	No. 3.	No. 4
Silicic Acid.....	46.5	46.5	46.8	45.1
Aluminium Oxide.....	39.5	36.4	36.8	35.0
Water.....	13.7	13.6	12.4	17.1
Potassium Oxide.....			0.3	
Calcium Carbonate.....	0.3	1.5	0.5	]2.7
Iron Oxide.....		1.2	].....	
Magnesium Oxide.....			]3.1	

Pure kaolin is white, usually more or less porous, and soft to the touch. When it is moistened with a small quantity of water and kneaded thoroughly, it forms a thick pasty mass which, when dried, becomes hard and of a pure white color. If it is triturated with a large volume of water, it becomes uniformly suspended in the liquid so that the mixture assumes the consistency of milk. Upon standing for

* Data from Dammer.

many hours, the kaolin settles upon the bottom of the containing vessel, as a pure white, amorphous, and perfectly non-elastic mass. Because of its softness and non-elasticity, the slightest pressure upon it leaves a permanent impress. It is to these properties that kaolin owes its value in the manufacture of porcelain and pottery.

330. Porcelain.—The difference between pottery and porcelain is in the quality of the kaolin which is used, only the finest and purest kinds being suitable for porcelain. When pure kaolin is heated to a high temperature, it forms a hard and flinty mass which will not fuse. When cooled, it forms an amorphous mass which may be pulverized to an impalpable powder. Such material is well adapted to form the body of porcelain, but it must be cemented together by some material which will withstand a higher temperature. It is found that a small quantity of feldspar exercises such a cementing effect. This is due to the fact that the pores of the kaolin become filled with feldspar, which fuses to a glass-like substance and thus binds the particles of kaolin together. The product is a hard, compact, porous, and more or less brittle mass. The second step consists in glazing the object by dipping it into a mixture which, when fired, fuses much more readily than the feldspar alone.

MANUFACTURE OF PORCELAIN

The manufacture of porcelain includes:

1. *Emulsifying the Raw Materials.*—This consists in grinding the kaolin and feldspar (or other cementing material) into an impalpable powder, and then churning it with much water until it is thoroughly mixed. The liquid is then allowed to stand until the suspended matter settles upon the bottom of the containing vessel.

2. *Drying the Emulsion.*—The sediment is then freed from its surplus moisture, either by natural evaporation or by exhausting the air in the containing vessel. This process reduces the material

to the consistency of a tough dough, which makes it ready for the potter.

3. *Shaping the Material.*—The shaping of the material is effected in various ways, two of which are especially effective:

a. The pasty mass is placed upon a rotating disk called a potter's wheel, and the workman fashions it into the desired shape with hands or tools.

b. Moulds are made of plaster of Paris, very thick-walled. The pasty material is mixed with water until it can be poured. The moulds are then filled with it and allowed to stand for some time. The plaster of Paris absorbs with great rapidity much of the water in the kaolin-paste. This causes some of it to adhere to the interior of the mould. The excess of the material is then poured out.

4. *Drying.*—The moulded object is then taken to the drying oven, where it is heated to about 30° , until it is quite dry, after which it is packed in an earthenware vessel, and placed in the kiln to be fired.

5. *Firing.*—The kiln is filled with the material, shaped as above, closed and fired. This process requires great care and attention, and usually lasts from 40 to 42 hours, after which the kiln is allowed to cool very gradually. The product is a hard, compact material which is technically known as "biscuit-ware." It must then be glazed and decorated.

6. *Glazing.*—If a plain porcelain is desired, the object is dipped into a tub of glaze whose composition depends upon the quality of the porcelain. For the hardest kinds, the glaze is made of very finely powdered feldspar of the purest kind uniformly suspended in water. For the common sorts, the glaze may be a mixture of feldspar, quartz, glass, etc. It requires great skill to dip the biscuit-ware so that the object will be uniformly moistened. The porous biscuit-ware quickly absorbs the moisture from the glazing material, which leaves a thin film upon the article. It is again placed in the kiln and fired. The second firing lasts only about fifteen hours, and the temperature is usually not so high as in the first firing. The second firing melts the glaze and converts it into a perfectly transparent glass.

7. *Decoration.*—In some of the cheaper sorts of porcelain, the decorations are designed in enamel colors upon paper, and bound to the biscuit-ware while the colors are still wet. The ware absorbs the ink, and the paper is then removed by water. These designs are then glazed and fixed by the second firing. The enamel colors are made of colored glasses ground to a fine powder and mixed with borax or some other material which melts easily to form a glaze. These colored glasses are silicates of certain oxides which are made by dissolving a quantity of the requisite oxide in melted glass

(p. 296). In the finer sorts of porcelain, the decorations are placed upon the glazed surface, and fixed by a third firing.

Finished porcelain is composed primarily of the silicates of aluminium, calcium, sodium, and potassium. The following table gives the composition of some of the celebrated varieties.

TABLE XLII*

	SiO ₂	Al ₂ O ₃	K ₂ O : Na ₂ O	CaO	Fe ₂ O ₃	MgO
Berlin Porcelain . .	66.6	28.0	3.4	0.3	0.7	0.6
Meissener.	59.4	32.6	5.5		0.4	
Sevres	58.0	34.0	3.0	0.4		
Chinese.	69.6	23.6	6.2	0.3	1.1	

331. Stoneware is a cheaper form of porcelain. It is made from a poorer quality of kaolin, and the cementing material used in preparing the "biscuit" is of a poorer quality, and more fusible, than the finer sorts of feldspar. A cheaper glaze is used, consisting of a mixture of clay, flint, lime, and borax (or some other similar materials). This yields a product which is not so hard and translucent as the harder kinds of porcelain.

332. Earthenware is made of clay which is a mixture of the silicate of aluminium, quartz, magnesium carbonate, calcium carbonate, etc. The method of preparing the "biscuit" is essentially the same as that for porcelain. In glazing it, common salt is thrown into the fire toward the close of the first firing. This is vaporized by the heat, and combines with some of the silicate of aluminium to form a good glaze. The articles are then cooled in the usual way.

*Data from Dammer.

333. Bricks are a very common variety of unglazed earthenware. The clay from which they are made is of the commonest sort, and often contains a great deal of calcium carbonate and the oxides of iron. The presence of these impurities determines the comparatively ready fusibility and the color of the bricks.

334. Ultramarine.—Before 1822, artists used a beautiful blue pigment which they obtained by pulverizing a costly ornamental stone, called *lapis lazuli*, or *ultramarine*. It was exceedingly expensive, retailing for from \$50 to \$60 per pound. Ultramarine is now made in enormous quantities from very cheap materials, and retails for about 10 cents per pound. It is used extensively as a dyestuff, in coloring wall-paper, in paints, etc.

Preparation.—When a mixture of clay, sodium sulphate, and charcoal is fused together, an intensely green compound is formed (ultramarine green), which is used as a pigment. When it is reheated with sulphur in the presence of air, it is changed to ultramarine blue. Violet and red ultramarines are also prepared and used as pigments.

THE BORON FAMILY

335. It was pointed out in the introduction to this chapter that the corresponding compounds of boron and aluminium are structurally alike, but that they differ in many of their chemical properties. Their structural similarity may be seen in the appended table. Note also that boron shows all of the fundamental attributes of a non-metal, and few of the attributes of a metal, while aluminium, on the other hand, shows few of the attributes of a non-metal, and practically all of the fundamental attributes of a metal. In this respect the two elements show a transition from the non-metals to the base-forming elements.

TABLE XLIII

PROPERTIES	BORON	ALUMINIUM
Specific Gravity.....	2.68 (crystalline) ..	2.56 (malleable).
Melting Point		700°.
Hydrogen Derivatives ..	BH ₃	Forms none.
1. Physical Properties	Gas	
2. Boiling Point.....		
Halogen Derivatives....	BCl ₃	AlCl ₃ ; Al ₂ Cl ₆ .
1. Physical Properties	Liquid	Solid.
2. Boiling Point.....	18°	193° (melting point).
3. Heat of Formation.	104 Cal.	321.9 Cal (Al ₂ Cl ₆).
4. Stability.....	Decomposes in water.....	Stable in water.
Oxygen Derivatives	B ₂ O ₃	Al ₂ O ₃ .
1. Physical Properties	Solid	Solid.
2. Point of Fusion....	577°	White heat.
3. Heat of Formation.	817.2 Cal. (Troost)	Al ₂ O ₃ , 3H ₂ O = 388.8 Cal.
4. Stability	Soluble in water..	Insoluble in water.
Acid Derivatives	$\left[\begin{array}{c} \text{H}_3\text{BO}_3 \\ \text{H BO}_2 \\ \text{H}_2\text{B}_4\text{O}_7 \\ \text{etc.} \end{array} \right]$	$\left[\begin{array}{c} \text{H}_3\text{AlO}_3 \\ \text{H AlO}_2 \\ \text{H}_2\text{Al}_2\text{O}_4 \end{array} \right]$
Properties.....	Stable in water...	Known only in combination; Al is essentially basic.
Salt Derivatives of monovalent Bases.....	$\left[\begin{array}{c} \text{M}_3\text{BO}_3 \\ \text{M BO}_2 \\ \text{M}_2\text{B}_4\text{O}_7 \\ \text{etc.} \end{array} \right]$	$\left[\begin{array}{c} \text{M}_3\text{AlO}_3 \\ \text{M AlO}_2 \\ \text{M}_2\text{Al}_2\text{O}_4 \\ \text{etc.} \end{array} \right]$

EXERCISES

1. Would a glass made of lead silicate be dissolved by fusing potassium carbonate?
2. What effect would a hot concentrated solution of baking soda have upon tinware?
3. Why does tinware "rust"?
4. Would the presence of a small quantity of copper, or iron oxide impair kaolin?
5. What is bisque ware?

6. Is Delft porcelain fundamentally different from other porcelains?
7. Why is water-glass a good cement for broken porcelain?
8. Is "china" a variety of porcelain?
9. How are paving bricks made?
10. What is "caustic" tiling? How is it made?
11. Outline the process for making "fire-brick."
12. What are the commercial qualities of aluminium-bronze?

CHAPTER XVIII

THE CHROMIUM GROUP: GROUP VI.

336. General Properties of Group VI.—It was pointed out in the introduction to Chapter XVII that the basic properties of the elements increase rather uniformly from the halogens through to the carbon group. The boron group is divided. Boron is more acidic than the elements of the carbon group, while aluminium is a well-defined base closely related to lead and tin of the carbon group. The boron group, therefore, bears no close relation to the preceding groups. There are two other elements whose relations to the preceding groups are also indefinite, namely, *chromium* and *manganese*. These elements possess many properties in common. Their lower oxides are basic in character, while the higher oxides are acid anhydrides. They are readily oxidized or reduced, their corresponding compounds are chemically and structurally similar, they form two classes of salts, the “ous” and the “ic”, and their salts possess about the same degree of stability.

CHROMIUM, CR (AT. WT. 52.1)

337. Occurrence of Chromium.—This interesting element does not occur free, and its natural compounds are neither plentiful nor widely distributed. Of these the most important is chromiron, $\text{FeO}:\text{Cr}_2\text{O}_3$, found in considerable quantity in Pennsylvania, Norway, Russia, etc. The free element may be prepared by reducing its oxide with charcoal, at a white heat.

338. Properties of Chromium.—Metallic chromium is a gray, amorphous, infusible powder, permanent in the air

under ordinary conditions, but slowly oxidized at a high temperature. It dissolves readily in hydrochloric acid, and in dilute hot sulphuric acid, with the evolution of hydrogen. This shows its basic character.

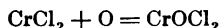
COMPOUNDS OF CHROMIUM

339. Halogen Derivatives.—There are two chlorine derivatives of chromium:

CrCl_2 , chromous chloride

Cr_2Cl_6 , chromic chloride

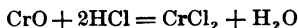
1. *Chromous Chloride* is a white, crystalline solid which dissolves readily in water, forming a blue liquid. The solution absorbs oxygen from the air and forms soluble chromium oxychloride,



2. *Chromic Chloride*, Cr_2Cl_6 , may be prepared by fusing an intimate mixture of chromic oxide and charcoal in an atmosphere of chlorine. It is a solid which sublimes in beautiful violet needles. It dissolves sparingly in water, forming a green liquid from which green crystals, $\text{Cr}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, separate when the liquid is concentrated.

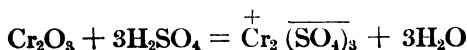
340. Oxygen Derivatives.—Chromium forms three oxides, CrO , Cr_2O_3 , and CrO_3 .

1. *Chromous Oxide*, CrO , is not well known. It is the oxide from which the chromous salts, such as CrCl_2 , are derived;

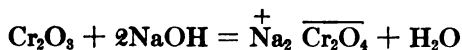


2. *Chromic Oxide*, Cr_2O_3 , is an amorphous green powder which is practically insoluble in water, and only sparingly soluble in acids.

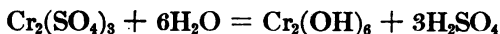
It shows the properties of a basic oxide and of an acid anhydride. As a basic oxide, it dissolves in strong acids to form salts;



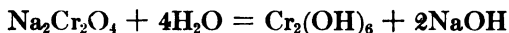
As an *acid anhydride*, it dissolves in a solution of sodium hydroxide, forming sodium chromite, $\text{Na}_2\text{Cr}_2\text{O}_4$.



Both types of compounds are unstable. The first has a tendency to decompose in much water;



The second is completely decomposed by boiling water into the hydroxides of sodium and chromium;



The salts of chromic oxide which contain crystal water are generally of a dark green color, and are sparingly soluble in water.

3. *Chromic Acid Anhydride*, CrO_3 , occurs in shining red crystals which dissolve readily in water, forming a strongly acid fluid which contains chromic acid, H_2CrO_4 .

341. Salts of Chromic Acid.—Chromium forms two important acids, neither of which is known in the free state: chromic acid, H_2CrO_4 , and pyrochromic or dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$. Their salts are stable compounds of great importance.

1. *Chromates*.—These salts are structurally like the sulphates. Potassium chromate, K_2CrO_4 , may be prepared by fusing chromic oxide or its salt with potassium nitrate and carbonate, and extracting the fused mass with water.

EXPERIMENT 76. Put about one gram of chromic oxide into a small crucible, and completely cover it with a mixture of one part of potassium nitrate and three parts of potassium carbonate. Cover and heat until the contents fuse and become homogeneous. Allow the crucible to cool, and digest its contents with water. An intensely yellow solution of potassium chromate will be formed.

Potassium Chromate is a yellow, crystalline solid which dissolves readily in water, forming an intensely yellow liquid.

When a soluble lead salt is added to this solution, yellow lead chromate is precipitated.

Lead Chromate is used extensively as a pigment in preparing yellow paint (chrome yellow), and in calico printing. When a solution of a chromate is acidified with sulphuric acid, it turns red from the formation of a dichromate;



2. *Potassium Dichromate*, the most important salt of dichromic acid, may be prepared by acidifying a strong solution of the chromate with sulphuric acid, and evaporating the solution to crystallization. The potassium dichromate crystallizes in beautiful red needles or plates which are soluble in about ten parts of water. The solution is red, has a very bitter astringent taste, and is poisonous. Potassium dichromate is used extensively for the preparation of other chromates in dyeing and calico printing, and as an oxidizing agent in the preparation of aniline violet and other dyestuffs.

342. Properties of a Mordant.—It has been found that many kinds of dyestuffs will not color woolen and cotton goods effectively until they have been dipped into a solution of alum, potassium dichromate, etc., and dried. After such treatment the dye is found to color the cloth uniformly. The substance which serves to fix the dye within the cloth, is called a *mordant*. A mordant has an affinity both for the cloth and the dye. Its effectiveness is perhaps due to its power to combine with water, wholly or partially, and form basic salts. Thus, when aluminium sulphate is used, it forms an insoluble salt within the meshes of the cloth. The cloth is then dipped into the dye, which immediately combines with the basic salt to form an insoluble, stable compound, thus fixing the dye. The power of a basic salt of aluminium to combine with organic coloring matter may be readily shown by Experiment 77.

EXPERIMENT 77. Dissolve two or three grams of aluminium sulphate in some water, make the solution slightly alkaline with ammonium hydroxide, let the precipitate settle, and wash it by decantation. Pour a test-tube full of litmus solution (or any other liquid which contains vegetable coloring matter) into the precipitate, add a little water, and let it stand a few minutes. On filtering, colorless liquid will be obtained.

343. Use of a Mordant in Pattern Making.—The art of printing designs upon cloth seems to have been practiced first at Calicut in India; hence the term “calico.” The action of a mordant in such work is well shown in the so-called “padding style” of stamping. The process is divided into three principal stages:

1. Suppose the cloth is to be dyed yellow, and a mordant of potassium dichromate used. The latter is finely pulverized and rubbed up to the consistency of a thick paste, with dextrin or gum arabic. A block which contains the pattern cut upon it in relief is then moistened with the mordant and the cloth is stamped.

2. It is then dried and washed carefully, after which it is immersed in a solution of lead nitrate or lead acetate containing approximately ten ounces of the salt to a gallon of water. This results in the formation of lead chromate within the fibers of the cloth which contained the mordant.

3. When the cloth is thoroughly washed and dried, the unchanged soluble lead salt is removed, but the lead chromate remains fast and firm.

There are many modifications of this process. At present many dyes are in use which do not require the use of a mordant.

344. Chemical Character of Chromium.—Chromium, like aluminium, is a base as well as an acid-forming element. Of its two oxides, Cr_2O_3 and CrO_3 , the former is basic, while the latter is an acid anhydride.*

* It will be shown in the succeeding pages that with many elements the acid properties of their oxygen derivatives seem to increase with rise in their percentage of oxygen.

MANGANESE, MN (AT. WT. 55)

345. Occurrence and Preparation.—This element, first isolated by Gahn in 1774, is found principally as pyrolusite, MnO_2 . Its affinity for oxygen is so strong that its oxide is reduced only with great difficulty. It is usually prepared by igniting a mixture of its dioxide and powdered coal or coke. The temperature rises very rapidly as the reduction proceeds.

346. Properties of Manganese.—The pure element is a white, lustrous, and infusible solid, permanent in dry air, but readily oxidized in moist air even at ordinary temperatures. In a finely divided state, it decomposes hot water with the evolution of hydrogen. It dissolves readily in acids to form salts, hydrogen being set free. It is so basic in character that it does not form a hydrogen derivative.

COMPOUNDS OF MANGANESE

347. Halogen Derivatives.—Manganous chloride, MnCl_2 , is a type of the halogen derivatives. It may be prepared by heating manganese dioxide with concentrated hydrochloric acid, filtering, and concentrating the filtrate until it crystallizes. It forms pink, monoclinic crystals.

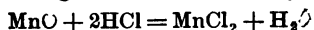
Manganic chloride, Mn_2Cl_6 , has not been prepared.

348. Oxygen Derivatives.—Manganese forms six well known oxides:

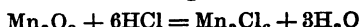
MnO , Mn_2O_3 , Mn_3O_4 , MnO_2 , MnO_3 , and Mn_2O_7

These oxides possess interesting chemical properties.

1. MnO is a *strong base*. It dissolves readily in acids to form the corresponding manganous salt, and hydrogen is set free;



2. Mn_2O_3 is a *very weak base*. It dissolves sparingly in acids, forming probably the unstable manganic salts;



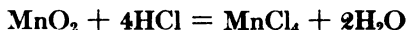
These salts decompose spontaneously into manganous salts;



8. Mn_2O_4 dissolves sparingly in acids, with which it forms the corresponding *manganous salts*. It is not dissolved by the hydroxides of sodium or potassium, which shows the absence of acid anhydride properties. It possesses, therefore, no distinctly basic or acid character.

4. MnO_2 is an indifferent oxide. It dissolves only in concentrated acids at high temperatures, forming the corresponding manganous salts (p. 54).

The first four oxides are to be construed as fundamentally basic in character, since they all form *manganous salts* when treated with the different acids. This seems to suggest that the normal valence of basic manganese is two. The *instability* of the manganic salts affords a simple explanation of the way the higher oxides behave toward acids. Thus it has been found that the dioxide and hydrochloric acid yield chlorine. If the normal valence of manganese toward the negative chlorine were four, no chlorine would be set free;



The valence, however, drops to two, with the following result:



A similar action takes place with sulphuric acid, the hot concentrated acid forming manganous sulphate and oxygen;

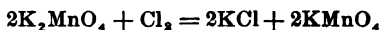


It follows that the higher oxides act usually as strong oxidizing agents.

5. MnO_2 is an amorphous, red solid which dissolves in water, forming a clear red liquid. The solution presumably contains manganic acid, H_2MnO_4 , which has never been isolated because of its instability. It is, however, a dibasic acid, and its alkali salts dissolve in water, forming a green solution.

EXPERIMENT 78. Place about 0.5 gm. of a manganese salt in a porcelain crucible, cover it with four times its volume of dry sodium carbonate, mix in 0.2 or 0.3 gm. of potassium nitrate, and fuse the mixture to a homogeneous liquid. A peacock-blue color will be formed, which is due to the presence of sodium manganate.

6. Mn_2O_7 is an oily, dark liquid which separates when cold, concentrated sulphuric acid is added to dry potassium permanganate. Paper, wood, alcohol, etc., ignite when dropped into it. This oxide is to be viewed as the anhydride of permanganic acid, HMnO_4 , a compound which has not been isolated owing to its instability, but whose salts, the permanganates, are stable compounds. The most important of these salts is potassium permanganate, KMnO_4 , which may be prepared by dissolving the manganate in water and passing chlorine into the solution;



349. Properties of the Permanganates.—The action of the permanganates upon other compounds is due to the tendency of permanganic acid to break up readily into manganese heptoxide and water;

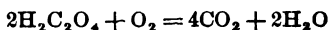


Its action, therefore, is the action of this oxide. The higher oxides of manganese dissolve in acids and form manganous salts. Manganous salts are derived from MnO ; hence the higher oxides are reduced to MnO , with the liberation of oxygen. When salts are formed from them the liberated oxygen may, of course, bring about some secondary reaction. When the solution of a permanganate is acidified, the acid is set free and decomposes into its anhydride and water. The anhydride is then acted upon by the excess of the acid, forming a manganous salt and nascent oxygen;



Hence permanganic acid or a permanganate will, when acidified, bring about the same chemical reactions as nascent oxygen. Two types of reactions occur:

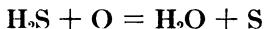
a. Suppose the solution in which the nascent oxygen is acting contains oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$. Oxygen has a great affinity for hydrogen and carbon. The acid will therefore be oxidized to water and carbon dioxide:



In general any compound whose elements have a strong affinity for oxygen will be decomposed and oxidized. Alcohol, starch, sugar, albumen, and other unoxidized carbon derivatives are thus acted upon. These compounds are endothermic, and by their oxidation to carbonic acid anhydride and water, considerable heat is set free.

b. Suppose the solution in which the nascent oxygen is acting contains a halogen acid. The halogens, excepting iodine, have slight affinity for oxygen, and the oxides which do exist are unstable compounds. In hydrochloric acid, e.g., we have a compound, one of whose elements has a strong affinity for oxygen, while the other has little or none. Nascent oxygen would oxidize the hydrogen to water, and the chlorine would be set free: $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$. Most compounds which contain hydrogen and a halogen will be oxidized, and the halogen liberated.

350. Uses of the Permanganates.—The ease with which potassium or sodium permanganate gives up its oxygen makes it a valuable disinfectant and cleansing agent. Thus, fermenting animal matter gives off hydrogen sulphide. The nascent oxygen from the permanganate immediately oxidizes it to water and free sulphur;



A dilute sulphuric acid solution of the permanganate is used in spraying gutters, sewers, and other places where fermentation is active.

351. Chemical Character of Manganese.—The chemical character of the six oxides of manganese and their deportment toward acids and bases indicate that manganese, like chromium, has a double nature; that is, it may act as a base or as an acid anhydride. The change in character of its oxides from a strong base to the neutral oxide, and then to an acid anhydride as the percentage of oxygen increases, is in harmony with the point made previously, that the acid properties of an oxide increase, usually, with the increase in its percentage of oxygen.

352. Chemical Character of Oxides Compared.—In the following table only those oxides are considered which have been isolated. Many strong oxidizing acids are known whose anhydrides have not been separated. If these hypothetical oxides were included, the acid tendency of the higher oxides would be more evident.

TABLE XLIV

	R ₂ O	RO	R ₂ O ₃	RO ₂	R ₂ O ₅	RO ₃	R ₂ O ₇
Chlorine....	weak acid.			acid			
Bromine....							
Iodine....					acid		
Sulphur....				weak acid.		strong acid.	
Selenium....				weak acid.			
Tellurium....				weak acid.			
Nitrogen....	neutral.	neutral	weak acid.	acid	strong acid.		
Phosphorus....			weak acid.		strong acid.		
Arsenic....			weak acid.		acid		
			very weak acid				
Antimony....			acid		acid.		
Bismuth....		neutral	basic		weak acid		
Carbon....		neutral		acid	weak acid		
Silicon....				acid			
Aluminium....			weak acid.				
Chromium....		neutral	weak acid.			strong acid.	
Manganese....		basic	weak base.	neutral		acid.	acid.

EXERCISES

1. Compare the chemical properties of Al₂O₃, and Cr₂O₃.
2. Would a solution of potassium dichromate deodorize decomposing vegetables? Why?
3. How may a flask be cleaned after it has contained amorphous carbon? Grease? Arsenic Sulphide?
4. How are the figures placed upon wall-paper?
5. What chemical effect would a solution of potassium permanganate have upon sodium arsenite? Sodium sulphite? Potassium nitrate?
6. Why does potassium permanganate color the fingers brown?
7. What effect would alcohol have upon a solution of permanganate?
8. Would chrom-alum be a good mordant? - Why?
9. How many grams of potassium chlorate are required to oxidize 0.3 grams of chromium oxide to chromic acid anhydride?
10. Compare the fundamental chemical properties of Al₂O₃, Cr₂O₃, and Mn₂O₃.

CHAPTER XIX

THE ALKALI-EARTH GROUP: GROUP VII.

The descriptive matter of the preceding groups shows that the elements in the first, second, and third groups have non-metallic, negative properties; while the oxides of the fourth and fifth groups show a transition from weakly acid anhydrides to feebly basic oxides. It has also been seen that the lower oxygen derivatives of chromium and manganese are basic, while their higher oxides are acid anhydrides. The members of the seventh group differ from the preceding groups in their chemical relations. This group comprises magnesium, calcium, zinc, cadmium, barium, strontium, and mercury. The chemical character of these elements is such that they are divided into two sub-groups, viz.; A. Magnesium, Zinc, Cadmium, and Mercury; and B. Calcium, Strontium, and Barium.

SUB-GROUP A

353. General Properties of Sub-Group A.—The elements of this group and their corresponding compounds possess many similar properties. They are all primarily dibasic; their chlorides, nitrates, and sulphates are soluble in water, while their oxides, carbonates, and phosphates are insoluble in water. Magnesium differs from the other elements in that its hydroxide is alkaline in reaction. This property gives it some relation to sub-Group B.

MAGNESIUM, MG (AT. WT. 24.36)

354. Halogen Derivatives.—For the preparation and properties of magnesium, see page 137. Of the halogen derivatives, the chloride is the most common. It is found in

sea-water, in some mineral waters, and in many minerals and rocks. It may be prepared by dissolving the carbonate in muriatic acid, and crystallizing the product. Magnesium chloride forms colorless, deliquescent crystals which contain six molecules of water. When magnesium chloride is heated strongly, it is decomposed into magnesium oxide and hydrochloric acid. It follows that water which contains this salt in solution is not suitable for iron steam boilers, on account of the corroding effect of the hydrochloric acid.

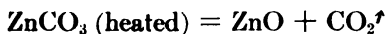
355. Oxygen Derivative.—Magnesium forms only one oxide, MgO , found sparingly in nature. It may be prepared by heating the carbonate to a high temperature, by which the carbonic acid anhydride is expelled, or by burning magnesium in oxygen. Magnesium oxide is a white, porous, and infusible powder, without odor and taste. It dissolves very sparingly in water, forming a feebly alkaline fluid which neutralizes acids, forming the corresponding salts of magnesium. The oxide is used extensively in medicine, as an ingredient of certain cements, and as a cleansing agent for brass, silver, gold, etc.

356. Other Salts of Magnesium.—The sulphate is found ready formed in nature in certain minerals, and in the waters of many springs, such as West Baden, French Lick, Baden Baden, Hunyadi Janos, Epsom, etc. It may be prepared by decomposing the carbonate with sulphuric acid and crystallizing the product. Magnesium sulphate is used in medicine and is called "salts," or "Epsom salts."

ZINC, Zn (AT. WT. 65.4)

357. Occurrence and Preparation.—This important element is not found free. Its chief compounds are the carbonate (*Smithsonite*, often known to the miners as "dry-bone")

and the sulphide (*sphalerite* or *zinc blende*), both of which are mined as ores. Their metallurgy is comparatively simple. The carbonate is first converted into its oxide by roasting;



The oxide is then reduced with coal to metallic zinc, and the free element is distilled at a high temperature. The sulphide is roasted in a current of air until it is changed to an oxide, which is then reduced. The reduction is carried on in earthenware tubes C (Fig. 69), which are connected with iron

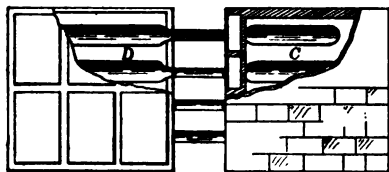


FIGURE 69

receivers D, into which the zinc vapor passes. The first portion of vapor is condensed to fine zinc dust by the comparatively cold walls of the receiver; but as the walls of the receiver become more heated,

it condenses to a liquid which is drawn off at intervals, and cast into bars or other shapes. These bars are then redistilled to free the zinc from lead, iron, and other impurities.

Zinc may be prepared in a chemically pure form by electrolyzing zinc chloride, the pure zinc separating at the negative electrode.

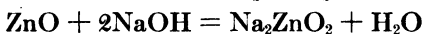
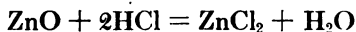
358. Properties of Zinc.—Zinc is a bluish-white, brittle solid at ordinary temperature, but when heated to 100° - 150° , it becomes so tenacious that it may be rolled into sheets or drawn into wire. Above 200° it again becomes brittle enough to be pulverized, and at about 500° it takes fire in the air and burns with a bluish-white flame, giving off copious white fumes of zinc oxide. It is insoluble in water, but it dissolves readily in mineral acids, with the evolution of hydrogen (p. 23).

359. Uses of Zinc.—Zinc is used extensively in the preparation of brass and other alloys. Galvanized iron is prepared by dipping the cleansed iron into a bath of molten zinc, and is used in the manufacture of netting, barbed wire, gutter pipes, etc. It is not readily attacked by water or dilute acids, and consequently does not easily corrode or rust.

•
COMPOUNDS OF ZINC

360. Halogen Derivatives.—The chloride and the iodide are of chief importance. The chloride, ZnCl_2 , may be prepared by dissolving the carbonate or oxide in hydrochloric acid, and evaporating the solution to dryness. It is a white, amorphous mass which absorbs water very readily. It is a powerful caustic to all albuminous tissue, and it is often used to cauterize chronic sores. Zinc iodide, ZnI_2 , prepared by heating a mixture of iodine and very finely divided zinc, is a brown pasty mass which is very hygroscopic. It is used in medicine as a local caustic, and as a remedy for inflammations.

361. Oxygen Derivative.—Zinc forms only one oxide, ZnO , which is one of the most important of the zinc derivatives. It is a white, amorphous powder which is insoluble in water, but dissolves readily in dilute acids, or strong caustic alkalis;



It is therefore a basic oxide, and also a weak acid anhydride. In this respect it resembles aluminium, chromium, and the other metalloids. It is prepared in large quantities by reducing zinc ores to metallic zinc, and burning the vaporized metal in a current of air. It is sold under the name "zinc white" for the preparation of white paint. Such paint gives a beautifully white surface, but it is likely to crack. This may in some measure be avoided by mixing it with "white

lead." Zinc oxide is also used in medicine in the preparation of the various zinc ointments.

362. Salts of Zinc.—Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, also called "white vitriol," is a white, crystalline solid which dissolves readily in water. It may be prepared by dissolving the metal or its oxide in dilute sulphuric acid, and crystallizing the product. It is made in commercial quantities by roasting zinc blende, ZnS , extracting the mass with water, and crystallizing. It is used in medicine as an emetic, and as a mild caustic.

CADMIUM, CD (AT. WT. 112.4)

363. Properties and Uses.—This element, discovered by Stromeyer in 1817, does not occur free, but is found associated with zinc in zinc blende and other minerals. The zinc ore is reduced with coal at as low a temperature as possible, whereby the cadmium, which boils at a lower temperature than the zinc, distills over and is purified. It is a white, lustrous metal which melts at 320° and boils at 760° . The density of its vapor is 56; therefore its molecule contains only *one* atom. It is used chiefly in the preparation of fusible alloys. Many of these alloys, of which "fusible metal" is the best example, melt at a low temperature. One variety of "fusible metal," which melts at a temperature of less than 100° , is an alloy of tin, lead, bismuth, and cadmium.

TABLE XLV*

	CADMIUM	LEAD	TIN	BISMUTH	MELTING POINT
Fusible Alloy	2	11	3	16	170° F.
" " 	10	8	3	8	167° F.
" " 	1	2	1	4	150° F.
Wood's Alloy	2	4	2	5	160° F.
Type-metal	22.5	50	36		

* Data from Hiorns. Other proportions are also used.

MERCURY, Hg (At. Wt. 200)

364. Occurrence and Preparation.—Mercury is found free to some extent, but its chief source is the sulphide, HgS , called *Cinnabar*. Cinnabar is found principally in Spain and California. It is reduced to metallic mercury by roasting it in pans placed in a central oven (Fig. 70), on either side of which are condensing chambers. The sulphur is separated, burned to sulphur dioxide and escapes; the metallic mercury distills over into the side chambers A A and is there condensed to a liquid.

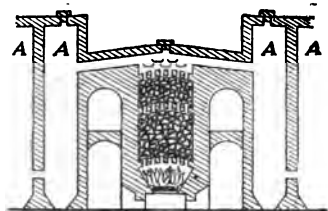


FIGURE 70

365. Properties of Mercury.—It is a silver-white metal (liquid) which possesses a remarkable luster. Its specific gravity is about 13.6; it does not change in the air; it boils at 357° and freezes at about -39.4° ; the density of its vapor is 100, and its molecule is therefore made up of one atom; it is slightly soluble in dilute hydrochloric or sulphuric acid, but dissolves readily in nitric acid.

366. Uses of Mercury.—Mercury is used extensively in the manufacture of thermometers and barometers, and in the metallurgy of gold and silver. It forms with other metals alloys called *amalgams*, which have a low melting point. An amalgam for making casts of fragile objects is composed of bismuth, 53.5 parts; lead, 17.0 parts; tin, 19.0 parts; and mercury, 10.5 parts. This alloy melts at 169° F, and remains liquid down to 149° F (Hiorns). An amalgam used by dentists contains 25.99 parts of cadmium and 74.01 parts of mercury. An amalgam of tin and mercury is used extensively in making

cheap mirrors. One method for their manufacture is to cover a perfectly smooth and level stone table with tin-foil, coat it several times with mercury, and then place the glass, which should be perfectly dry and clean, upon it, and press it vigorously against the amalgam. The amalgam adheres to the glass, making it a mirror.

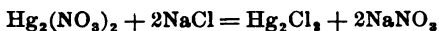
COMPOUNDS OF MERCURY

367. Halogen Derivatives.—Mercury forms two series of halogen salts;

Hg_2R_2 , mercurous salts

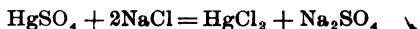
HgR_2 , mercuric salts

1. *Mercurous Chloride*, Hg_2Cl_2 , may be prepared by precipitating a solution of mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$, with a soluble chloride, such as sodium chloride;



It forms a white, heavy precipitate, insoluble in water and acids. Moistened with dilute ammonium hydrate, a black mass is formed. Mercurous chloride may be sublimed by heating it over the free flame. It then forms a hard white mass which may be powdered, and is known in medicine as "calomel."

2. *Mercuric Chloride*, HgCl_2 , called "corrosive sublimate," may be prepared by heating metallic mercury in chlorine gas, or by subliming a mixture of mercuric sulphate and common salt;



The sodium sulphate remains as a fixed residue and the mercuric chloride sublimes into a white, crystalline mass. It dissolves readily in water or alcohol, forming a colorless liquid which is extremely poisonous. A water solution of corrosive sublimate (usually 1 : 1000) is used extensively in surgery because of its powerful antiseptic properties.

3. *Mercuric Iodide*, HgI_2 , is readily prepared by precipitating it from a solution of mercuric chloride with potassium iodide. It is an amorphous, scarlet powder, insoluble in water and acids but readily soluble in an excess of potassium iodide. It is used extensively in medicine as a remedy for inflammation, and as a specific in certain blood and skin diseases.

4. *Mercurous Iodide*, Hg_2I_2 , is a yellow powder which possesses less commercial and medicinal value than the corresponding mercuric salt.

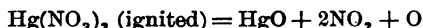
368. Oxygen Derivatives.—There are two oxygen derivatives of mercury;

Hg_2O , mercurous oxide

HgO , mercuric oxide

1. *Mercurous Oxide* is precipitated when a solution of mercurous nitrate is made alkaline with potassium hydroxide. It is a brown-black powder which is insoluble in water, and is very unstable, breaking up readily into metallic mercury and mercuric oxide.

2. *Mercuric Oxide* occurs in two forms, yellow and red. The red oxide is formed when mercuric nitrate is heated in a sand-bath until dissociation takes place;



It is a basic oxide, uniting with the acids to form stable salts. Heat dissociates it into metallic mercury and oxygen (p. 108). The yellow oxide, which possesses essentially the same chemical properties, is precipitated when a solution of mercuric chloride is made alkaline with potassium or sodium hydroxide.

369. Other Compounds of Mercury.—Mercuric Sulphide, HgS , is an amorphous, black powder which is insoluble in water and acids. A brilliant red modification of it, called “vermilion,” may be obtained by subliming the black mercuric sulphide, or by subliming a mixture of metallic mercury and sulphur. It is used extensively in making a fine quality of red paint called “vermilion red.”

Mercurous Nitrate, $\text{Hg}_2(\text{NO}_3)_2$, is formed when 1 part of metallic mercury is dissolved in 1.5 parts of cold nitric acid (25 per cent). It crystallizes in colorless crystals which are decomposed by heat into mercuric oxide and nitrogen dioxide.

Mercuric Nitrate, $\text{Hg}(\text{NO}_3)_2$, is prepared by dissolving metallic mercury in hot, concentrated nitric acid.

Mercuric Sulphate, HgSO_4 , made by heating a mixture of four parts of metallic mercury and five parts of strong sulphuric acid until complete solution takes place, is a crystalline substance which is decomposed by much water into sulphuric acid and a yellow basic salt.

Fulminating Mercury, $\text{HgC}_2\text{N}_2\text{O}_8$, is a compound of mercuric nitrate and alcohol. It is used in the manufacture of gun-caps.

370. Sub-Group A.—The similarity between the elements of Sub-Group A and their corresponding derivatives, and

the variation of their attributes with changes in atomic weight, seem to justify their arrangement in a group. These relations may be more clearly seen in the following table.

TABLE XLVI

	MAGNE- SIUM	ZINC	CADMIUM	MERCURY
Atomic Weight..	24.36.....	65.4.....	112.4.....	200.....
Melting Point...	800°.....	417°.....	320°.....	-39.4.....
Specific Gravity.	1.75.....	7.1.....	8.6.....	13.6.....
Chlorides.....	MgCl ₂	ZnCl ₂	CdCl ₂	HgCl ₂
H. of F.	151 Cal.....	97.2 Cal.....	93.2 Cal.....	63 Cal.....
Oxides.....	MgO.....	ZnO.....	CdO.....	HgO.....
H. of F.	151 Cal.....	85.4 Cal.....	65.4 Cal.....	30.6 Cal.....
Sulphates.....	MgSO ₄	ZnSO ₄	CdSO ₄	HgSO ₄
H. of F.	302 Cal.....	230 Cal.....	231 Cal.....	
Sulphides.....	MgS.....	ZnS.....	CdS.....	HgS.....
H. of F.	Mg, S=79.6 Cal.	Zn, S, Aq=41.5 Cal.	Cd, S, Aq=34 Cal.	Hg, S = 16.8 Cal.

SUB-GROUP B

(The Alkali-Earth Group of Elements)

371. General Character of Sub-Group B.—The three most important members of this group are Barium, Strontium, and Calcium. These elements and their corresponding derivatives possess striking similarities. The elements are all true metals, which are hard, ductile, and fusible with difficulty. They oxidize readily in moist air, and they decompose water, forming the corresponding hydroxides, and liberating hydrogen. Therefore hydrogen is always given off at the negative electrode (cathode) when their salts are electrolyzed. These elements are diads, and they do not form hydrogen derivatives. Calcium is the most abundant and important.

CALCIUM, CA (AT. WT. 40.1)

372. For the preparation and properties of calcium, see page 138.

COMPOUNDS OF CALCIUM

373. Halogen Derivatives.—Calcium is such a strong base that it replaces the hydrogen in the halogen acids under ordinary conditions, forming the corresponding salts. These salts are solids which dissolve readily in water. Some of them absorb water on exposure to the air, becoming liquid. They are then said to deliquesce.

Calcium chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, the most important salt of this series, is a colorless compound which loses its water of crystallization at 200° , and is changed at 720° , to a white, amorphous mass called "fused calcium chloride." This salt possesses a great affinity for water, and is in consequence much used for drying gases and solids (p. 14).

374. Oxygen Derivatives.—Calcium forms two oxides;

CaO , calcium monoxide

CaO_2 , calcium dioxide

375. Calcium monoxide is commonly called "quick-lime." It does not occur free, but is made by heating the carbonate in a current of air;



It is prepared for commercial purposes by burning broken limestone in large furnaces called lime-kilns. The kilns (Fig. 71), are usually somewhat cylindrical in shape and lined with fire-clay. The broken limestone is so placed in them that at base it forms a low arch, under which the fire is kindled and allowed to burn until all of the carbon dioxide is expelled from the limestone. Usually about twelve hours are required to complete the expulsion of the CO_2 . The kiln is allowed to cool, and the calcium oxide is placed in barrels which are then closed.

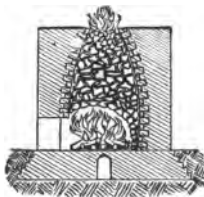
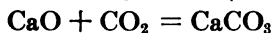
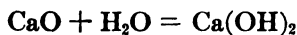


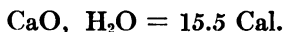
FIGURE 71

Pure calcium oxide is a white, amorphous, infusible substance which becomes intensely luminous when heated to a high temperature. This property is utilized in the Drummond, or lime-light, in which light is made by directing a short, colorless, and intensely hot flame, usually obtained by the combustion of hydrogen in pure oxygen, against a cylindrical bar of compressed calcium oxide.

On exposure to the air, quicklime absorbs both moisture and carbonic acid and forms a white, fine powder. It is then said to be air-slaked. The product is a mixture of the hydroxide and the carbonate of calcium;



376. Slaked Lime: Calcium Hydroxide.—When a quantity of calcium oxide is treated with one-half its weight of water, the water is first absorbed, and then chemical activity becomes so energetic that much heat is evolved and steam escapes. This is due to the formation of calcium hydroxide. The energy relations may be seen from the heat of formation of the hydroxide from the oxide;



Calcium hydroxide is a white, fine powder which dissolves in about 800 parts of water, forming a very strongly alkaline liquid called "limewater." A relatively small proportion of water combined with calcium oxide forms a thin white paste called "milk of lime," which is one of the chief constituents of mortar.

377. Mortar.—Mortar consists usually of about one part of milk of lime to which three or four parts of sand have been added. It becomes very hard on long exposure. The chemistry of this change is not well known. The fundamental change

consists in the loss of water, and the absorption of carbonic acid anhydride, CO_2 , by which calcium hydroxide is changed to hard calcium carbonate. The sand probably facilitates this change by keeping the mortar porous and thus allowing a freer contact of air.

The speed with which the mortar hardens, or "sets," depends largely upon the composition of the lime. The lime of commerce is rarely pure. It almost always contains more or less silicate of aluminium, carbonate of magnesium, as well as other impurities. The coarseness and composition of the sand also has some influence on the "setting" of the mortar. When the lime has such composition that the mortar made from it sets quickly under water, the mortar is called hydraulic mortar, cement, or "water lime."

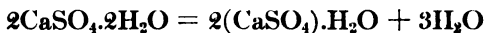
378. Cements.—A. *Portland Cement.* It was early discovered that lime, which is prepared by calcining limestone that contains about ten per cent of silica, will harden under water. This property is utilized to-day in the manufacture of cements. Chief among these is "Portland Cement." Limestone and clay (or impure limestone of the proper composition) are mixed with water and ground to a very fine powder. The powder is then dried and burned in a furnace to expel the carbon dioxide and moisture. The product will combine with water to form a hard, insoluble, compact mass. The chemical processes which cause the cement to harden are not understood. The following analyses of Portland cements show their average composition.

TABLE XLVII*

SAMPLES	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SiO_2	SO_3	S	H_2O
White Brothers	59.0	0.8	6.9	3.4	0.7	0.9	24.1	1.6		...
English	54.1	0.8	7.8	5.3	1.1	1.6	22.2	1.0		1.00
French	60.9		7.4	4.5			25.4			
German	62.0	1.1	6.5	2.8	0.6	1.7	22.6	1.2		

*Data from Schmidt.

B. Plaster of Paris.—This is another type of cement that is used in putting the finishing touches, or “skim coat,” on rough plaster. It is made from gypsum (hydrated calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The gypsum is finely ground, and heated to about 130° , whereupon it loses three-fourths of its water of crystallization;



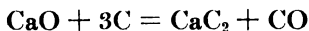
The product, called “Plaster of Paris,” is a white, amorphous mass which, when mixed with the proper proportion of water, forms a creamy mixture which “sets” quickly to a hard, compact mass. The hardening is due to the re-absorption of water;



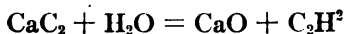
If it is spread with a trowel during the hardening, it forms a smooth and more or less glossy surface. Plaster of Paris is well adapted to moulding casts and statuary, because it expands when hardening, and thus gives a sharp reproduction of the object.

379. Other Compounds of Calcium.—For the properties of calcium phosphate, see page 232; for the properties of calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, see page 194.

Calcium Carbide, CaC_2 (p. 247), is a white, crystalline solid when pure, but the commercial calcium carbide is reddish or gray, the color being due to the presence of impurities. It is manufactured on the large scale by heating calcium oxide and coke in an electric furnace;



It is decomposed by water into calcium monoxide and acetylene, C_2H_2 ;



ACETYLENE

380. Preparation.—Acetylene is a hydrocarbon in which two carbon atoms are bound together by six bonds; $\text{HC}\equiv\text{CH}$. It is formed when an electric spark strikes between two carbon electrodes which are suspended in an atmosphere of hydrogen. It is also formed during the incomplete combustion of the lighter hydrocarbons. Thus, when the flame from a bunsen burner "strikes back" and burns at the base, incomplete combustion ensues and acetylene is given off. The peculiar odor which emanates from such a flame is due to the presence of this gas.

381. Properties of Acetylene.—Acetylene is a colorless, poisonous gas, with an offensive, penetrating odor. It may be liquefied under a pressure of 48 atmospheres and a temperature of $+1^\circ$. The liquid is colorless and explosive, especially when a flame is brought near it. Acetylene combines with the salts of certain metals, as copper, mercury, and silver, and forms explosive compounds called acetylides. Thus, cuprous salts and acetylene give a red precipitate which has the formula Cu_2C_2 . Acetylene is a strongly *endothermic* compound, its heat of formation from the elements being -47.7 Cal. From the ordinary gas jet, acetylene burns with a smoky flame; but when it is mixed with air in a suitable burner before combustion, it yields a brilliant white light. Such a burner is shown in Fig. 72. The arms are placed at such an angle that the gas which issues from BB' will be deflected perpendicularly. The openings at CC' are connected respectively with BB' so that the air is drawn in through these apertures and mixed with the acetylene before it issues from BB' . Acetylene light resembles sunlight, and most colors appear the same as in daylight. One pound of calcium carbide will produce about five cubic feet of gas, sufficient to supply a "one-half foot burner" for ten hours. Such a burner will, it is claimed, produce a light equal to that from thirty-two stearine candles. Since one pound of the carbide costs about five cents, the cost of a thirty-two candle power light per hour would be one-half cent. The small cost of the plant, and the steadiness and brilliancy of the acetylene flame commend this method of illuminating where coal gas cannot be obtained.

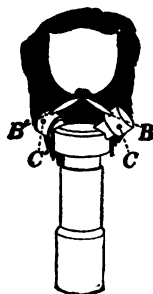


FIGURE 72

BARIUM, BA (AT. WT. 137.4)

For the Preparation and Properties of Barium see page 143.

COMPOUNDS OF BARIUM

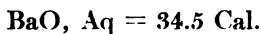
382. Halogen Derivatives.—These are similar to the corresponding salts of calcium.

383. Oxygen Derivatives.—Barium combines with oxygen in two proportions;

BaO, barium monoxide

BaO₂, barium dioxide

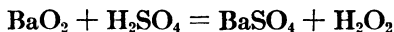
1. *Barium Monoxide* is a gray, amorphous mass which may be readily obtained by heating the nitrate of barium. It combines with water with the evolution of much heat, and forms barium hydroxide;



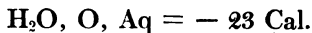
It is transformed into the dioxide at a dull red heat;



2. *Barium Dioxide* is a white powder which closely resembles the monoxide in its physical properties. When it is treated with sulphuric acid, insoluble barium sulphate is precipitated, and *hydrogen peroxide* remains in solution;



The precipitate is filtered off, and the filtrate is concentrated in vacuo to a small volume. This solution, which is the *hydrogen peroxide* of commerce, is a clear liquid which has a pungent and slightly bitter taste, and decomposes spontaneously into water and oxygen; it is therefore a strong oxidizing agent. This instability is indicated by the equation,



It is used extensively as a disinfectant and germicide, and as a mild bleaching agent. It is especially adapted to the cleansing of wounds, ulcers, abscesses, etc.

384. Barium Sulphate, BaSO_4 , familiarly known as "heavy spar," is found in nature in rhombic prisms which are about five times as heavy as water. It may be prepared by treating a soluble barium salt, such as the chloride, with dilute sulphuric acid and filtering off the precipitate. Thus prepared it is a white, amorphous powder, practically insoluble in water and acids, and used extensively as a substitute for "white lead" in the manufacture of paints.

STRONTIUM, SR (AT. WT. 87.6)

385. Properties and Uses of Strontium.—For its preparation and properties see page 143. It is a much rarer element than calcium. Its oxygen and halogen derivatives are very similar, both physically and chemically, to the corresponding compounds of barium and calcium. The soluble salts of strontium impart a very intense crimson color to a flame, and because of this property they are extensively used in fireworks. This property may be shown as follows: Carefully dry and pulverize 2 gm. each of potassium chlorate and strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, add 1 gm. of shellac, which has been powdered separately, mix the three ingredients intimately, place the mixture under the hood, and fire it with a match or red-hot wire. When $\text{Ba}(\text{NO}_3)_2$ is substituted for the $\text{Sr}(\text{NO}_3)_2$, the powder gives a green flame.

THE ALKALI-EARTH FAMILY

386. General Properties.—The members of this group are called the "alkali-earth" metals because they possess attributes which are similar to those of the alkali metals and the earth metals (aluminium, iron, etc.). Thus the oxides are white infusible solids, and in this respect they are similar to the oxide of aluminium. They dissolve in water, forming a strongly alkaline fluid, and this property is also possessed by the alkali metals.

In general, the attributes of the different types of derivatives show similar variations with increase in the atomic weight of the elements. Thus, calcium carbonate is readily decomposed by heat into its oxide and carbonic acid anhydride; strontium carbonate gives up its acid less readily, and barium carbonate is only slightly decomposed even at a white heat. The same gradation is observed in the solubility of the sulphates and chlorides. The calcium compounds are the most soluble,

TABLE XLVIII

	CALCIUM	STRONTIUM	BARIUM
Atomic Weight.....	40.1	87.6'	137.4
Specific Gravity....	1.6.....	2.50	3.75
Oxides.....	CaO.....	SrO	BaO
H. of F.....	130.7 Cal...	128.4 Cal...	124.2 Cal.
The Chlorides	CaCl ₂	SrCl ₂	BaCl ₂
1. Solubility in 1000 cc. of water at 50°.	41200 gm ...	744 gm.....	437 gm.
2. H. of F.....	170.2 Cal ..	184.5 Cal...	194.20 Cal.
The Sulphates	CaSO ₄	SrSO ₄	BaSO ₄
1. Solubility in 1000 cc. of water at 50°.	2.56 gm....	0.28 gm.....	.02 gm.
2. H. of F.....	318.3 Cal ..	330.8 Cal...	337.5 Cal.
The Carbonates....	CaCO ₃	SrCO ₃	BaCO ₃
Dissociation Temp..	600° C	1100° C	1400° C
The Hydroxides....	Ca(OH) ₂ ...	Sr(OH) ₂ ...	Ba(OH) ₂
Solubility in 1000 cc. of water at 50°....	1.37 gm.....	7.98 gm.....	38.81 gm.

the barium salts the least so, while the strontium salts stand between those of calcium and barium. The similarity in the properties of the elements and their corresponding derivatives, and the relation of their attributes to the atomic weights of the participating elements have led to their grouping into a natural family. These facts are emphasized by the foregoing table.

Summary.—The members of Group VII show an interesting relation to the preceding groups. It was pointed out in Table XL that the basic properties of the elements, as there arranged, increase from left to right, and from the top downward. It was also pointed out in Chapter XVIII that chromium and manganese serve as transitional elements; that is, they may act either as true bases or as acid anhydrides. The relation of the atomic weights of the seventh group of elements to the atomic weights of the other elements will be seen in the following table.

TABLE XLIX

A E	I AT. WT.	B E	II AT. WT.	C E	III AT. WT.	D E	IV AT. WT.
F.....	19.....	Cl...	35.45..	Mn..	55.....	Br...	79.96..
O.....	16.....	S.....	32.06..	Cr...	52.1....	Se...	79.2...
N.....	14.04..	P.....	31.....			As...	75.....
C.....	12.....	Si.....	28.4....				
B.....	11.....	Al.....	27.1....				
.....		Mg...	24.36..	Ca...	40.1....	Zn...	65.4...

E E	V AT. WT.	F E	VI AT. WT.	G E	VII AT. WT.	H E	VIII AT. WT.
.....		I.....	126.85..				
.....		Te...	127.6...				
.....		Sb...	120.2...			Bi....	208.5
.....		Sn...	119.....			Pb....	206.9
.....							
Sn....	87.6...	Cd...	112.4..	Ba...	137.4..	Hg...	200

It was also pointed out in the preceding pages that the elements of Group VII do not form hydrogen derivatives. This fact points to their basic character, and this interpretation is confirmed by the fact that their oxygen derivatives, excepting ZnO , do not behave as anhydrides *even when associated with the caustic alkalis*. Group VII is, as a whole, more basic in character than any of the preceding groups, and Sub-Group B is more basic than Sub-Group A. This is to be observed in the properties of the hydroxyl derivatives. Those of Group A are neutral in reaction, while those of Group B are *very strongly alkaline*. Thus it may be said that *the basicity of the elements increases with marked regularity from fluorine to barium, when the elements are grouped as in Table XLIX*.

EXERCISES

1. What is "zinc white"? White vitriol?
2. What is galvanized iron? Why does it not rust?
3. What effect would hot potassium hydroxide have upon it?
4. Of what is the "zinc" made, which is placed under stoves?
5. Will the products from the combustion of illuminating gas discolor "zinc white" paint?
6. Why does "vermilion" paint gradually turn yellow?
7. Compare the chemical properties of ZnO and HgO .
8. What are the chemical properties of calcium oxide which make it a good material for the preparation of mortar?
9. Could aluminium oxide be substituted for it? If not, why not?
10. What is stucco?
11. What are the fundamental differences between cements and porcelain?
12. What are the products of the combustion of acetylene?
13. Would barium oxide be a good substitute for calcium oxide in preparing mortar?
14. How many grams of acetylene in 22.25 liters at N.T.P.?
15. How much calcium carbide will be required to prepare 22.25 liters of acetylene measured at N.T.P.?

CHAPTER XX

THE ALKALI GROUP OF ELEMENTS: GROUP VIII.

THE RELATION OF GROUP VIII TO THE PRECEDING GROUPS

It is the purpose of this chapter to discover the relations which obtain between the elements in Group VIII and those of the preceding groups.

Group VIII is made to include Lithium, Sodium, Potassium, Rubidium, Caesium, Copper, Silver, and Gold. It may be divided into two sub-groups: A. Lithium, Sodium Potassium, Rubidium, and Caesium; B. Copper, Silver, and Gold.

The division is based upon the fact that the two sub-groups are somewhat unlike in their chemical properties, while the elements which make up a sub-group are very similar. Thus, all the elements of Sub-Group A possess a strong affinity for oxygen; those of Sub-Group B have a very *slight* affinity for that element.

SUB-GROUP A

(*The Alkali Metals*)

387. General Properties of Sub-Group A.—The elements of this sub-group are very similar in their physical and chemical properties, and so are their corresponding compounds. The free elements are soft, waxy solids with a true metallic luster; they are lighter than water (excepting caesium and rubidium), and they combine with water with great energy, forming a hydroxide, and liberating hydrogen. This reaction is often so violent as to become explosive. The hydroxides are solids which dissolve in water, forming a strongly alkaline

solution. They are called the "caustic alkalis." The elements are powerful univalent bases. They replace the positive hydrogen of acids, forming salts which are usually stable. *Their salts with weak acids give the alkaline reaction.*

LITHIUM, Li (At. Wt. 7.03)

388. Occurrence and Properties.—This element, first isolated by Davy by electrolyzing its fused chloride, does not occur free, and its compounds are found only in small quantities. It occurs in some minerals, and in many mineral springs, such as Baden-Baden, Carlsbad, Buffalo Lithia Springs, etc. It is a silver-white, soft metal of 0.59 specific gravity, whose salts, with the exception of the carbonate and

phosphate, are soluble in water. Some of them find a limited use in the arts, and in medicine.

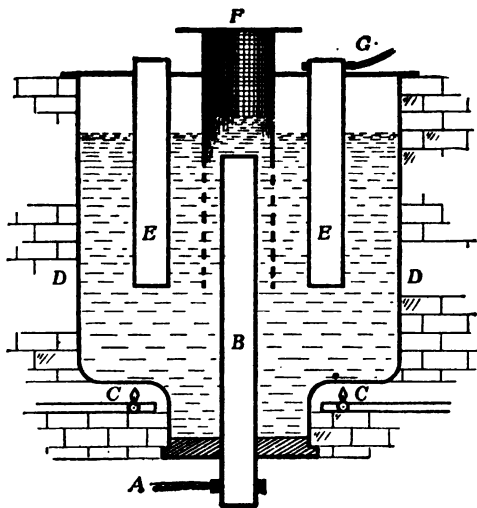


FIGURE 73

SODIUM, Na (At.
Wt. 23.05)

389. Preparation of Sodium.—

For the method of preparation and properties of sodium, see page 135. Sodium is now prepared in commercial quantities by

the electrolysis of fused sodium hydroxide.

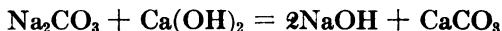
One form of apparatus is shown in Fig. 73. D is an iron cylinder which rests upon a brick shoulder and is heated by the flames CC. These keep the sodium hydroxide in the upper part of the cylinder

D in a liquid state, but that in the neck remains solid. EE and B are heavy iron bars which serve respectively as positive and negative electrodes. The cylinder F is wrapped in a wire gauze which dips into the fusing caustic soda.

Process.—The large cylinder D is filled with sodium hydroxide which is melted by the flames CC. A strong electric current is then passed through the liquid from EE to B. The sodium separates at B and collects in the cylinder F, but it is kept from mixing with the liquid caustic soda by the wire gauze. Some hydrogen also collects in F, and prevents the sodium from oxidizing. The separated sodium is either ladled out from F, or drawn off through a side tube not shown in the illustration.

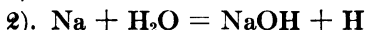
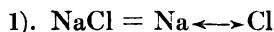
COMPOUNDS OF SODIUM

390. Preparation and Properties of Sodium Hydroxide.—Sodium hydroxide, NaOH, is prepared in commercial quantities by two processes, one of which consists in boiling slaked lime with sodium carbonate. Thus a boiling solution of ten parts of sodium carbonate in ten parts of water is treated with a mixture of three parts of calcium oxide in ten parts of water, added in small portions;



The calcium carbonate is insoluble and separates as a white precipitate. The filtrate contains the sodium hydroxide, which may be obtained by evaporating the solution to dryness in an iron or silver dish.

The other process consists in the electrolysis of a concentrated solution of sodium chloride. When a very strong solution of common salt is exposed to the influence of the electric current, it is decomposed with the formation of sodium hydroxide, hydrogen, and chlorine:



One form of apparatus is shown in Fig. 74. It consists of a rectangular box B which is divided into three parts by the partitions DD', which extend nearly to the bottom. Mercury is poured into the

box until it rises above the lowest point of the partitions D D' and thus makes each division impervious to liquids. The carbon

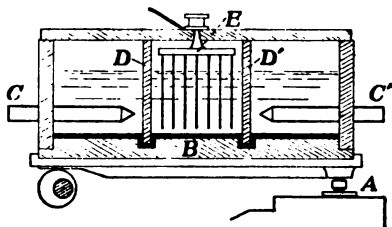
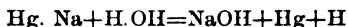


FIGURE 74

electrodes C C' are immersed in a solution of sodium chloride, and E (the negative electrode) dips into pure water.

Process.—When the electric current passes into the salt solution from the carbon electrodes, it must pass through the bed of mercury before reaching the electrode E, because the partitions D D'

are made of material which is a non-conductor. The surface of the mercury thus acts as an electrode. The current separates the salt into chlorine and sodium, the chlorine rises to the surface of the liquid in the outer compartments and escapes, and the sodium forms an amalgam with the mercury (p. 60). By rocking the apparatus very gently on the point A, the liquid mercury-sodium amalgam is caused to flow into the central compartment, where it is acted upon by the water, forming sodium hydroxide, metallic mercury, and hydrogen:



The hydrogen escapes through the opening in the top of the central compartment, and the sodium hydroxide dissolves in the water and is drawn off. The solution is evaporated to dryness and the residue is melted and cast into sticks.

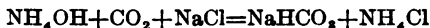
The fused hydroxide is a white, crystalline substance which possesses great affinity for water; consequently it liquefies speedily when exposed to moist air.

Sodium hydroxide is extensively used in the arts, sciences, and in the manufacture of materials for domestic purposes. It is an indispensable reagent in the chemical laboratory, and is consumed in large quantities in making soap (p. 276), paper, cotton goods, and many washing preparations.

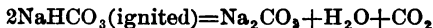
391. Preparation of Sodium Carbonate.—Sodium carbonate, Na_2CO_3 , may be viewed as the hypothetical carbonic acid, H_2CO_3 (p. 145), in which the two positive hydrogen

atoms have been replaced by sodium. It is prepared commercially by two well-known processes, the Solvay and the Le Blanc.

a. The Solvay Process is based upon the fact that sodium hydrogen carbonate, NaHCO_3 , is formed when a solution of common salt in aqueous ammonia is saturated with carbonic acid anhydride;



The sodium hydrogen carbonate is but sparingly soluble and is precipitated as a white powder. It is then separated, dried, and ignited;



b. The Le Blanc Process uses sodium chloride as the source of its sodium, and calcium carbonate as a source of carbonic acid anhydride. The process includes three fundamental steps:

1. The salt is transformed into sodium sulphate on being heated with strong sulphuric acid. One form of the apparatus in which the process is carried on is shown in Fig. 75. The crude sodium chloride

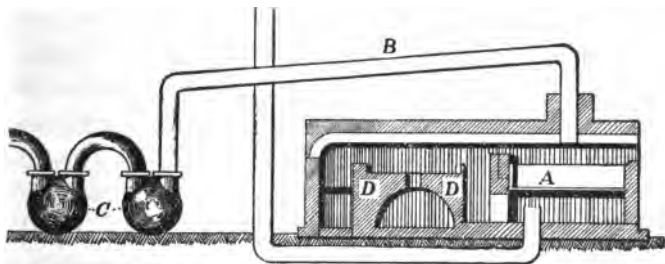
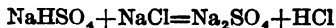


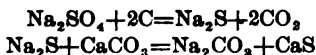
FIGURE 75

is placed in the chamber A, an equal weight of commercial sulphuric acid is added, and the mixture is gently warmed. The salt is decomposed into sodium hydrogen sulphate and hydrochloric acid; $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$. The hydrochloric acid passes through the tube B into the receivers C, which are half filled with water for dissolving the acid fumes. When fumes of hydrogen chloride cease to come off, the residue in A is raked through into chamber D D, where it is heated to dull redness. This heating serves to transform the remaining acid sodium sulphate and sodium chloride into sodium sulphate and hydrogen chloride;



The vapor of hydrochloric acid distills over and is dissolved in the water in the receivers. This is the principal source from which the hydrochloric acid of commerce is obtained.

2. The crude sodium sulphate is mixed with an equivalent quantity of powdered calcium carbonate, and 0.7 its quantity of coal. The mixture is then heated in a reverberatory furnace (p. 120) until it fuses to a more or less homogeneous mass. A double decomposition takes place;



3. The black mass is then digested thoroughly with water, which dissolves the sodium carbonate, and the evaporated solution yields crystals of sodium carbonate, which, when calcined, constitute the soda-ash of commerce.

392. Properties of Sodium Carbonate.—Sodium carbonate (salsoda) crystallizes in large, colorless prisms which contain 10 molecules of crystal water. On exposure to dry air, it quickly loses its crystal water (effloresces) and is changed to a fine white powder. It dissolves readily in water, forming a strongly alkaline liquid. It is one of the most important of the sodium salts, since it is extensively used in chemical laboratories, in pharmacy, and in the arts, especially for the manufacture of sodium silicate.

393. Sodium Bicarbonate, "Baking Soda," NaHCO_3 , may be prepared by saturating a hot solution of sodium carbonate with carbonic acid anhydride. It is a fine white powder, which is used in baking and in the preparation of baking powders (p. 259).

POTASSIUM, K (At. Wt. 39.15)

394. Preparation and Properties.—For the preparations and properties of potassium, see page 136.

COMPOUNDS OF POTASSIUM

395. Halogen Derivatives.—These salts crystallize in cubes. They may be prepared severally by neutralizing the

hydroxide or carbonate with the corresponding halogen acid, and evaporating the liquid until a residue crystallizes. The bromide and iodide are used in medicine and in photography.

396. Other Salts of Potassium.—*Potassium hydroxide* is very similar to sodium hydroxide in its properties. It is manufactured in the same way and appears in the trade in the same form.

Potassium carbonate is very much like sodium carbonate. Formerly it was obtained by leaching wood-ashes with water, and evaporating the liquid (called lye) to dryness in iron pots. Hence the name "potash." Its presence in wood-ashes is accounted for by the fact that many rocks, from whose decomposition-products the soil was made, contained compounds of potassium. These compounds are taken up by the plants and form part of their structure. When plants are burned, the potassium combines with escaping carbon dioxide and forms the carbonate. At the present time, large quantities of the carbonate are made from potassium chloride or potassium sulphate by the Le Blanc process.

Potassium nitrate, KNO_3 , is found in the soil and is produced from decaying refuse organic matter. When organic compounds are exposed to warmth and moisture, they undergo the nitrofying fermentation; that is, the albuminous molecules are decomposed, and the nitrogen is oxidized to nitric acid. The potassium which is present combines with it to form potassium nitrate. At present large quantities are made by treating sodium nitrate, Chili saltpeter, NaNO_3 , with crude potassium chloride. The two salts are mixed in equi-molecular quantities, dissolved in water, and evaporated to a small volume. When the solution reaches a definite degree of concentration, the common salt crystallizes out. Afterward, the more soluble potassium nitrate crystallizes out in long prisms. The dry salt is extensively used in the laboratory,

and as an oxidizing agent in the preparation of gunpowder (p. 227).

RUBIDIUM, Rb (At. Wt. 85.4); CAESIUM, Cs (At. Wt. 133.0)

397. Occurrence and Properties.—These two exceedingly rare elements are found associated with potassium in some minerals. The salts which they form are similar to the corresponding salts of potassium, but have only a theoretical interest.

THE ALKALI FAMILY

398. General Properties.—The similarity in the physical and chemical properties of these elements was referred to in the introduction to this chapter. The ammonium radical, NH_4 , is generally included in the group because its salts are closely related to the corresponding salts of these elements. It is a fact that the chemical activity of the respective elements increases successively from lithium to caesium. There is also a like regular variation in the specific gravity, and a reverse relation in the melting points. These and other facts which led to their grouping into a natural family are brought out in the following table.

TABLE L

ELEMENTS	ATOMIC WEIGHT	SPECIFIC GRAVITY	MELTING POINT	CHLORIDE MCL	SULPHATE M_2SO_4	NITRATE MNO_3
Lithium....	7.03	0.59	180°	LiCl	Li_2SO_4	LiNO_3
Ammonium	18			NH_4Cl ..	$(\text{NH}_4)_2\text{SO}_4$	NH_4NO_3
Sodium....	23.05	0.97	95.5°	NaCl ...	Na_2SO_4 ...	NaNO_3
Potassium..	39.15	0.87	62.5°	KCl	K_2SO_4	KNO_3
Rubidium..	85.4	1.52	38.5°	RbCl ...	Rb_2SO_4	RbNO_3
Caesium....	133.0	1.88	26.5°	CsCl ...	Cs_2SO_4	CsNO_3

EXERCISES

1. What are "effervescing lithia tablets"?
2. What is "concentrated lye"?
3. Why is it kept in iron boxes?
4. Why is it serviceable in removing grease spots?
5. Test the reaction of several "washing powders."
6. What are "salts"? Glauber's Salt?
7. Compare the chemical properties of Na_2O , CaO , Al_2O_3 , P_2O_5 .
8. How may dried linseed oil be removed from clothing?
9. Will paint resist the action of potash-lye?
10. What effect would "concentrated lye" have upon varnish?

CHAPTER XXI

GROUP VIII—(*Continued*)

SUB-GROUP B; COPPER, SILVER, AND GOLD

399. General Properties of Sub-Group B.—The elements of this group (all of which occur free) have been known since ancient times. Silver and gold are not affected by oxygen at any temperature. Copper combines with it slowly at ordinary temperatures, more rapidly at high temperatures. Copper oxide is readily reduced to metallic copper (p. 112). Although these elements show less basic activity than the metals of the alkalis and alkali-earths, they are true metals. This is to be noted in their fine luster, their extraordinary ductility and malleability, and their power to conduct heat and electricity. Their compounds possess certain similarities, though these are not striking.

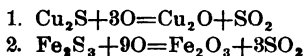
COPPER, Cu (At. Wt. 63.6)

400. Occurrence of Copper.—Copper is found in the free state about Lake Superior, and in Chili, Spain, Australia, etc. The red oxide, Cu_2O , the black oxide, CuO , Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and copper pyrites, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, are also important minerals from which the metal copper is obtained.

401. Preparation of Copper.—The metallurgy of copper is very important and involves many perplexing problems. Most of its ores contain small quantities of arsenic, antimony, lead, bismuth, and often tin and silver. These are reduced in its manufacture and are alloyed with it. The most objection-

able of these are arsenic, antimony, and small quantities of the unreduced cuprous oxide, for they are apt to make the copper hard and brittle. The method used for the reduction of the ore depends upon the character of the ore. The following are the fundamental points in the Welsh process as outlined by Sexton. The Welsh ores are a mixture of copper pyrites, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, iron pyrites, FeS_2 , and silicates.

1. *Roasting the Ore*.—About three tons of the crushed ore are heated in a reverberatory furnace for from 12 to 24 hours at a low temperature. The principal chemical changes are:



The roasted ore is then raked through the floor into the open space below.

2. *Melting for Coarse Metal*.—About three tons of the roasted ore are placed in a reverberatory furnace and melted. Some of the ore is reduced, and the coarse metal, which contains about 30 per cent of copper, mixed with iron and sulphur, is drawn off.

3. *Roasting the Coarse Metal*.—The coarse metal obtained in (2) is again roasted in a reverberatory furnace to transform it into the oxides of the elements which are present.

4. *Melting for White or Blue Metal*.—A charge of coarse metal is mixed with slag, and some oxide or sulphide of copper, and the charge is again melted. The molten mass is then drawn off. It is white or blue, depending upon the quantity of sulphur or iron present. The "white metal" is nearly pure cuprous sulphide, and has a steel-white color.

5. *Roasting for Blister Copper*.—Four or five tons of the white metal (Cu_2S) are placed again in the reverberatory furnace and the charge is slowly heated to the melting point, with free access of air. The sulphur is burned out and the melted copper is drawn off. The product is about 99 per cent copper.

6. *Refining of Blister Copper*.—About ten tons of the 99 per cent copper are placed in a reverberatory furnace and melted down. Air is allowed free access, by which the sulphur and iron are oxidized. Some of the copper is oxidized to cuprous oxide, which dissolves in the molten copper. This must be reduced, otherwise the copper will be brittle. All slag is raked off, and coal or charcoal is added. The carbon and any carbon monoxide then effect the reduction of the cuprous oxide to metallic copper.

402. Electrolytic Purification of Copper.—The copper which is prepared by the Welsh and other reduction processes usually contains from 0.5 to 2 per cent of impurities, such as arsenic, silver, bismuth, etc. These objectionable metals may be removed by electrolyzing the crude copper. The

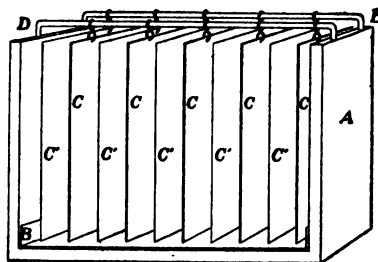
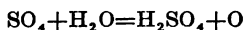


FIGURE 76

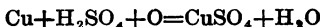
crude copper is drawn directly from the smelter and moulded into plates about 1 meter long and 0.5 meter wide. They are then purified by the apparatus shown in Fig. 76. A is a wooden vat made of pitch-pine; C-C are the plates of crude copper which serve as positive electrodes, or *anodes*;

C'-C' are very thin plates of chemically pure copper of the same shape and size as the crude plates, and which act as negative electrodes, or *cathodes*. These two sets of plates are placed in the electrical circuit by the copper rods D and E. B is a pan made of sheet lead, which collects any impurities which may separate from the anodes and settle to the bottom of the vat.

Process.—The vat is nearly filled with a solution of copper sulphate acidified with sulphuric acid, the plates are placed as shown in the cut, and a current (which varies from 1.8 to 9.3 amperes per square foot) is passed from C to C'. Soluble copper sulphate is separated into Cu^+ and $\overline{\text{SO}}_4^-$. The Cu^+ migrates to and is deposited upon the cathodes C'-C'. The $\overline{\text{SO}}_4^-$ collects at the anodes, where it unites with the water and liberates oxygen (p. 156);



The nascent oxygen and the regenerated sulphuric acid dissolve a corresponding quantity of copper from the impure anodes C-C



The copper which is withdrawn from the solution and deposited upon the cathodes will be replenished, atom for atom, by pure copper from the impure anodes, and thus the process is continuous.

The impurities in the anodes do not dissolve in the sulphuric acid, and when the copper which surrounds them is dissolved out, they separate and settle to the bottom, where they are collected by the leaden pan B. This mud which collects in the pan is worked over for any silver which it may contain.

403. Properties of Copper.—Pure copper is a reddish (copper colored), malleable, and ductile solid, which melts at about $1,280^{\circ}$. It does not change in dry air, but in moist air it becomes coated with a green basic carbonate, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$. It is not easily attacked by dilute acids. Hot, concentrated nitric acid dissolves it readily, copper nitrate being formed.

404. Uses of Copper.—Copper is used in the manufacture of electrical appliances, for electrical wiring, for copper vessels, sheeting for roofs, and for the preparation of alloys. Among the alloys are:

TABLE LI*

	COPPER	ZINC	TIN	LEAD	IRON	ALUMIN- IUM
Brass	66 . . .	34 . . .				
Watch Wheels	60.66.	36.88.	1.35.		0.74.	
Brass Nails	62.62.	24.64.	2.64.	8.69.		
Dutch Alloy	76.00.	24.00.				
Hard Solder (for brass)	50.00.	50.00.				
Bronze	91.39.		8.38.			
Gun Metal (Prussian)	90.91.		9.09.			
Small Bells	40.00.	60.00.				
Aluminium Bronze . . .	67.00.	31.75.				1.25

The above analyses represent *types* of alloys. Each type has a number of kinds, whose attributes vary with the proportion of their constituents.

* Data from Hiorns. Other proportions are also used.

COMPOUNDS OF COPPER

405. Halogen Derivatives.—There are two types of these derivatives: Cu_2R_2 and CuR_2 . The two chlorides are the most important of these salts.

1. *Cuprous Chloride*, Cu_2Cl_2 , made by boiling cuprous oxide in strong hydrochloric acid, is a white, crystalline compound which dissolves sparingly in water.

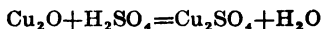
2. *Cupric Chloride*, CuCl_2 , prepared by dissolving cupric oxide in hot, concentrated muriatic acid, forms green crystals which contain two molecules of water.

406. Oxygen Derivatives.—Copper forms two oxides;

Cu_2O , cuprous oxide

CuO , cupric oxide

1. *Cuprous Oxide* is a red, crystalline powder, insoluble in water, but soluble in the stable mineral acids, forming cuprous salts;



It is prepared by boiling a solution of copper sulphate and grape sugar which has been made very strongly alkaline with sodium hydroxide.

2. *Cupric Oxide* is formed when copper nitrate is strongly ignited, or when copper is heated in an atmosphere of oxygen (p.46). It is a brown-black solid, insoluble in water, but soluble in acids, forming cupric salts.

407. Salts of Copper.

1. *Copper Sulphide*, CuS , is a black solid which is formed when a soluble salt of copper is treated with hydrogen sulphide.

2. *Copper Nitrate*, $\text{Cu}(\text{NO}_3)_2$, is a blue solid which is very soluble in water.

3. *Malachite* is a native carbonate of copper which possesses a beautiful green color. It is extensively used in ornamental stone work.

4. *Copper Sulphate*, $\text{CuSO}_4 + 5\text{H}_2\text{O}$, also called "blue vitriol," is one of the most important salts of copper, and is used extensively as a germicide, in preparing blue and green pigments, in copper-plating, etc.

ELECTROPLATING AND ELECTROTYPING

408. General Process.—Electroplating and electrotyping consist primarily in bringing about the deposition of a thin coating of metal upon a given surface.

I. Electroplating.—The object to be plated is thoroughly cleansed, suspended in a solution which conducts the electric current, and made the cathode. The anode is made of the metal to be deposited, and is of about the same area as the object to be plated. Thus, if it is desired to plate a piece of iron with copper, the iron is made the cathode, and a copper plate of approximately the same area is the anode, and both are suspended in a solution* of copper salt. The current should pass for from ten to twelve hours.

Copper plating has found a wide application in the arts. It is used extensively in plating fine woodcuts and other delicate objects, because it gives an exact mould of the object that is hard and resistant.

The American Postal Telegraph Company is now using steel wires which have been plated with copper. A series of copper baths have been arranged, through which the wire is passed until the deposit of copper is sufficiently heavy. The baths are supplied with the current from 25 large dynamos. This plant is capable of depositing 500 lbs. of copper per mile upon 20 miles of steel wire in about 60 hours (M'Millan).

II. Electrotyping.—In electrotyping, a cast is first obtained by pressing against the type or the cut to be electrotyped, a material such as gutta-percha (or a mixture of gutta-percha, lard, and tallow), wax, or other suitable material which is capable of taking accurate impressions.

*Solutions of varying strength have been suggested. One which has given satisfactory results contains, for example, 1.5 pounds of copper sulphate and 0.5 pounds of concentrated sulphuric acid dissolved in one gallon of distilled water. This solution gives excellent results with a current of 1 ampere per square decimeter of cathode. This is equivalent to about 3 amperes per 100 sq. inches of surface in the cathode plate. Since the current from an ordinary gravity cell, flowing through a short distance, e.g. 1 cm. of electrolyte, gives approximately 0.2 ampere strength, then an object ten inches square would require about 35 such cells.

The second step consists in rendering the mould conductive. This is done by brushing finely ground graphite into every detail of it. The mould is then made the cathode in the plating bath, and the process of depositing the copper is carried on as outlined in electroplating. When the deposited copper is thick enough, e.g., .01 inch, the process is stopped. This is the positive, or facsimile reproduction of the original object.

SILVER, AG (AT. WT. 107.93)

409. Occurrence and Preparation.—Silver is found in nature free and in compounds. among its principal ores are silver sulphide, Ag_2S , and silver chloride, AgCl . These are usually mixed with other minerals. The metallurgy of silver is the basis of a very important industry. Free silver ores and the chloride ores are especially adapted to the “amalgamation process,” which consists of six fundamental steps, as follows: crushing, pulping, panning, settling, distilling, and purifying.

A general arrangement of the machinery for carrying out the process is shown in Fig. 77. A is a crushing mill which

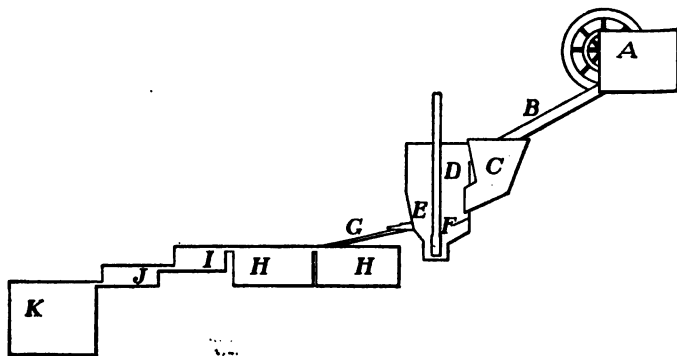


FIGURE 77

is not unlike the stone crusher used in preparing macadam. B is a chute for leading the coarsely crushed ore into C,

C is an automatic feeder which is so arranged as to distribute a uniform fall of the crushed ore into the mortar D. The shaft F is a heavy iron rod whose upper end is connected with a shaft driven by steam, and which is so arranged as to give to the shaft F a tamping motion. H H are wooden boxes. I is the amalgamating pan, and J the settler, similar in construction to the amalgamating pan.

Process: 1. Crushing the Ore.—The large pieces of ore are thrown into the crusher A, which reduces them to small lumps. The crushed ore is fed into the chute, which leads it to the automatic feeder C, by which the ore is fed uniformly into the mortar.

2. *Pulping the Ore.*—The ore from A is reduced to a fine powder by the stamp F. Water is run into the mortar simultaneously and, flowing out through the side of the mortar E, carries with it over the bridge G into the boxes H H, the ore which is finely powdered. In these boxes the coarser particles are collected, while the slime which remains suspended is carried away and collected in reservoirs, or discarded. The settlings, which contain most of the silver, are then transferred to the amalgamating pan, I.

3. *Amalgamating the Ore.*—The settlings from the boxes H H are thoroughly pulverized in the amalgamating pan I. From 60 to 70 pounds of mercury are then added to the ore in the pan, and the grinding is continued for an additional two hours, during which the silver combines with the mercury (the compound is called an amalgam) and is thus withdrawn from the pulp and remains in the pan because it is much heavier than the pulp.

4. *Settling the Amalgam.*—The pulp and amalgam are transferred to the settler J, in which they are mixed with a large volume of water. The pulp is washed out, but the heavy amalgam settles. The box K serves to collect any amalgam that is washed from the settler.

5. *Distilling the Amalgam.*—The amalgam, from which most of the sand and other mechanically mixed particles have been removed, is strained through canvas or leather bags in order to extract as much of the surplus mercury as possible.

The cleansed amalgam is then placed in small iron pans lined with several layers of paper to prevent the amalgam from forming an alloy with the iron. The pans are then introduced into a large iron retort A, Fig. 78. The retort is usually cylindrical. The end opposite the feed door is tapped by a pipe B, which is surrounded, throughout a portion of its length, by cold water. This pipe serves to condense the vapor of mercury into a liquid which is collected in the mercurial cistern C. The feed door is made gas-tight and a slow fire is kindled

under the retort. The temperature is slowly raised until it reaches 357° , at which temperature the mercury is vaporized, and this temperature is maintained for about two hours. It is then increased to bright

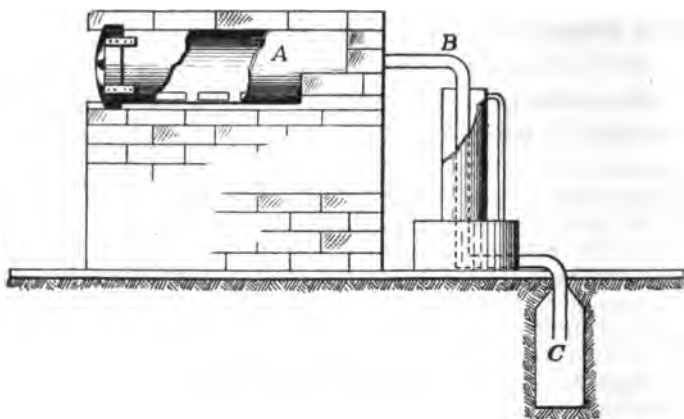


FIGURE 78

redness to remove the last portions of the mercury by evaporation. The iron pans are then withdrawn, and the silver residue, which contains from 50 to 90 per cent of silver, is removed. The residue also contains gold, a little mercury, and a small percentage of base metals.

6. *Purifying the Crude Silver.*—The silver may be separated from any gold by heating the residue in concentrated sulphuric acid, which dissolves out the silver. The silver may also be separated by electrolysis. See *Gold*.

410. Properties of Silver.—Silver is a white metal of remarkable luster, capable of taking a fine polish. It melts at a temperature of $1,000^{\circ}$. It does not combine directly with oxygen even at a red heat, and hence its surface is not oxidized on exposure to the air. It combines readily with sulphur to form black silver sulphide; hence articles of food which contain sulphur, such as albumen, generally blacken silverware. Silver is not attacked by dilute hydrochloric or sulphuric acid, but it dissolves readily in nitric acid, and in concentrated boiling sulphuric acid. It is also appreciably soluble in potassium cyanide.

411. Uses of Silver.—The uses of silver are well known. It is extensively used in the manufacture of tableware, jewelry, and other ornaments, for silver coins, mirrors, wire, crucibles, and reagents for laboratory purposes.

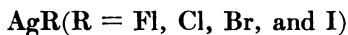
412. Alloys of Silver.—Pure silver is too soft to resist rough usage. It is therefore alloyed with some other metal, usually copper, to give it hardness. Silver coins and “sterling silver” are examples. The following table shows the composition of certain coins:

TABLE LII*

ALLOYS	COPPER	SILVER	ZINC
British Coins or Sterling Silver.	75	925	
French Coin.....	100	900	
American Coin.....	100	900	
Silver Solders.....	25	800	175

COMPOUNDS OF SILVER

413. Halogen Derivatives.—Silver shows a strong affinity for the halogens, with which it combines to form compounds of the general type;



The salts may be prepared by precipitating a solution of silver nitrate with the corresponding halogen acid or its alkali salt. These halogen derivatives are insoluble in water or dilute acids, but fairly soluble in ammonia, potassium cyanide, and sodium hyposulphite. They are readily decomposed when exposed to the light, part of the halogen being set free, and metallic silver separated. This property is made use of in photography.

*Data from Hiorns.

414. Photography.—A glass plate which has been coated with gelatin that contains a halogen salt of silver, such as silver bromide, is exposed in a camera to the light from the object to be photographed. The silver salt is in part decomposed, the degree of decomposition being proportional to the intensity of the light and the duration of the exposure. Thus a dark object will give out few light rays, and that part of the plate exposed to these rays will be but little affected. A white surface will reflect practically all of the light, and hence the part of the plate which these rays strike will be largely affected. The relative intensities of these effects are brought out by washing the plate with a reducing agent, such as pyrogallic acid (the developer), by which the *partly decomposed silver salt is reduced to metallic silver*. The depth of the silver deposit is thus proportional to the intensity of the light upon the original plate. The figure upon the plate is now the reverse of the object, and is called a “negative” (Fig. 79). The plate still contains that portion of the original silver



FIGURE 79

salt which has not been acted upon by the light or the developer. This must be removed before the negative is exposed to the light; otherwise it, too, will be acted upon as above described and the negative will be blurred. This is done by washing the plate in a solution of sodium hyposulphite (thiosulphate). This treatment is said to “fix” the negative. It is now permanent to the light, and is ready for the printing. This is done by allowing the sunlight to fall through the negative upon a sheet of sensitized paper. The *dark spots* upon the

negative represent the *light* parts of the object. It follows that the print will have the *same* shading as the object. The print is then



FIGURE 80

“fixed” by removing the unchanged silver salt. The print is therefore the *positive* of the original object (Fig. 80).

415. Oxygen Derivatives of Silver.—Silver does not combine directly with oxygen. Two oxides, Ag_2O and Ag_2O_2 , may be prepared by indirect methods.

Silver oxide, Ag_2O , is a dark brown amorphous powder, and Ag_2O_2 is a black, unstable solid. Both oxides of silver dissolve in acids, forming salts of the general type AgR , in which R is a monobasic, negative radical.

416. Salts of Silver.—1. *Silver Nitrate*, AgNO_3 , is the most important salt of silver. It is a white, crystalline solid which is a strong caustic. It is extensively used in medicine under the name “lunar caustic.”

2. *Silver Sulphide*, Ag_2S , is a black solid which may be prepared by passing hydrogen sulphide through the solution

of a silver salt. Its attributes are essentially the same as those of copper sulphide.

GOLD, AU (At. Wt. 197.2)

417. Occurrence and Preparation.—Gold occurs widely distributed over the earth, both native and combined. The native gold is usually mixed with compounds of copper, silver, or iron. It is found diffused through other minerals, especially in quartz veins and in the sands which have resulted from the disintegration of gold-bearing rocks. There are two standard processes of mining gold, dependent on its mode of occurrence. There are: (A) placer mining and (B) mining in solid rock.

A. Placer mines are those in which gold is washed out of gravel and sand. In hydraulic placer mining, heavy streams of water are directed against the gravel beds. The water, carrying the gravel and gold-bearing sand, is led into a series of troughs so arranged that there is a swift current, whereby most of the dross is washed away while the gold and silver, being heavier, settle to the bottom. The gold is then purified by amalgamating it with mercury, as outlined in B. The chief impurity is silver, from which the gold may be freed by rolling it into thin sheets and boiling them with concentrated sulphuric acid. This dissolves the silver, and leaves the gold, which is dried and then fused with carbon and sodium carbonate.

B. When gold ore occurs in solid rock, it is often in veins. In vein mining, the gold-bearing mineral (usually quartz) is taken from the mine, and the gold extracted from it by the amalgamating, the chlorination, or the cyanide process. Amalgamation is adapted to ores which contain free gold, unmixed with a high percentage of sulphides, while the other two processes are better adapted to the separation of gold from low-grade ores rich in sulphides. The amalgamat-

ing process may be divided into five fundamental steps: crushing, pulping, amalgamating, distilling, and purifying.

A general scheme for the arrangement of the machinery for prosecuting the work is shown in Fig. 81. A, C, and E respectively are a rock crusher, an automatic feeder, and a mortar, which are practically

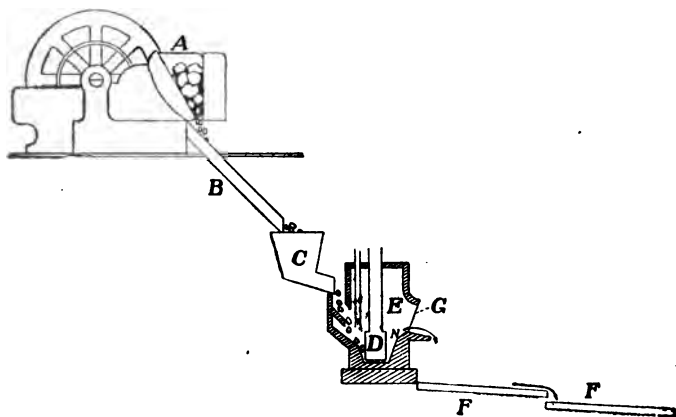


FIGURE 81

the same in construction as those used in the metallurgy of silver. The mortar E usually has an additional brass plate N, which is about 3 in. wide and as long as the mortar. F F are wooden tables which are as wide as the mortar (about 5 ft.) and approximately 7 ft. long.

Process: 1. *Crushing the Ore.*—The ore from the mine is screened to separate the finely divided part from the coarse lumps. The finely divided ore is run directly into the automatic feeder C, but the coarse lumps are fed into the crusher A, where they are ground into smaller pieces. The crushed ore is carried by the chutes into the feeder C, by which in turn it is distributed to the mortar.

2. *Pulping the Ore.*—The coarse ore is reduced to a fine pulp by the shaft-head D. During the pulping, a stream of water is directed against the shaft above the point D. The water keeps the steel head clean, and carries off the pulp through the screen G, to the tables F F.

3. *Amalgamating the Ore.*—The pulp falls upon the amalgam plate F, and is floated over its surface toward the second plate F, where it is again exposed to amalgam. These tables are so arranged that the water which transports the pulp tumbles over the surface of the plate in wavelets and thus brings practically all of the pulp into

contact with the amalgam. By this treatment practically all of the free gold is amalgamated with the mercury and is thus fixed upon the surface of the table. As the absorption (amalgamation) of the gold takes place, the surface of the table becomes so hard that additional quantities of mercury must be rubbed into it. Great care must be taken to keep the amalgamated surface in a more or less pasty condition, otherwise the gold will not be completely extracted from the pulp. When a sufficient quantity of gold amalgam has accumulated upon the plate N and the surface of the tables, the mill is stopped and the amalgam is scraped off the plates.

4. *Distilling the Amalgam.*—The apparatus and process for distilling the gold amalgam is essentially the same as that outlined for silver (p. 375).

5. *Purifying the Gold.*—Silver is usually the chief impurity found in the gold residue. It may be separated from the gold by strong sulphuric acid, as outlined on page 376, or by electrolysis. This method is essentially the same in principle as that used in the purification of copper (p. 370).

418. Properties of Gold.—Gold is a bright yellow metal which does not combine directly with oxygen at any temperature. It is exceedingly heavy, its specific gravity being about 19.3. It is malleable and ductile to a remarkable degree. It is very inactive chemically, but it dissolves slowly in aqua regia, forming gold trichloride, AuCl_3 .

419. Uses of Gold.—Pure gold is too soft for practical use, hence it is alloyed with some other metal, usually copper or silver. Gold coins of the United States are alloys of 9 parts of gold and 1 part of copper. In Great Britain the proportions are 11 parts of gold to 1 part of copper. The purity of gold for jewelry and other wares is usually measured in carats, pure gold being 24 carats fine.

COMPOUNDS OF GOLD

420. Gold is so indifferent in its chemical affinity that its compounds are few and unstable.

1. It forms two chlorides, AuCl and AuCl_3 . Of these two salts, the trichloride is the more important. It is formed when the free element is dissolved in aqua regia. The chlorine can be readily withdrawn by reducing agents. When a solution of gold chloride is treated with stannous chloride, a purple-colored precipitate is formed, known as "Purple of Cassius," which consists of finely divided gold.

2. There are three oxides, Au_2O , AuO , and Au_2O_3 . They are prepared by indirect methods.

3. Gold sulphide, Au_2S_3 is a brown-black solid, obtained by treating the chloride in solution with hydrogen sulphide. Its chemical properties are very similar to those of silver sulphide.

THE SUB-GROUP B

421. The preceding discussion of these elements and their derivatives will make clear the grounds for grouping them into a natural family. Their physical and chemical relations may be seen in Table LIII.

TABLE LIII

	COPPER	SILVER	GOLD
Atomic Weight.	63.6.....	107.93.....	197.2
Specific Gravity.	8.5-8.88.....	10.42-10.57.....	19.3
Melting Point...	1054° (?).....	1023° (?).....	1245°
Chlorides.....	CuCl_2 ; Cu_2Cl_2	AgCl ; Ag_2Cl	AuCl_3 ; AuCl
Oxides	CuO ; Cu_2O ...	Ag_2O_2 ; Ag_2O	Au_2O ; AuO ; Au_2O_3
Sulphides.....	CuS ; Cu_2S ...	Ag_2S	Au_2S_3

EXERCISES

1. Why does vinegar turn copper vessels green?
2. What is "blue vitriol"? For what is it used?
3. Could a flower be electroplated?
4. Why does silverware tarnish?
5. What does it signify when a piece of silverware is said to be "sterling silver"?
6. How could stains made by lunar caustic be removed?
7. How many grams of pure gold in 13.0 gm. of an 18-carat alloy?
8. Will hydrogen sulphide tarnish gold?
9. How could the silver be extracted from a dry mixture of silver salts?
10. What is "white metal"?
11. What would be a suitable solder for gold and silverware?

CHAPTER XXII

THE IRON GROUP OF ELEMENTS: GROUP IX.

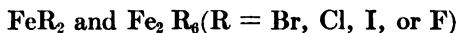
422. General Properties.—The members of this group are iron, nickel, and cobalt. These elements are similar in their physical and chemical properties. They are magnetic, they form “ic” and “ous” derivatives, their oxides are not acid anhydrides, they combine with cyanogen, forming complex negative radicals, they do not form hydrogen derivatives, their salts are stable compounds, etc.

IRON, Fe (At. Wt. 55.9)

423. Preparation, etc.—For the source, preparation, and properties of iron, see page 113.

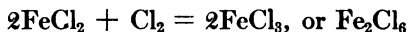
COMPOUNDS OF IRON

424. Halogen Derivatives.—Iron combines with the halogens in two proportions,



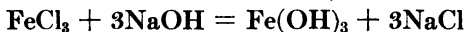
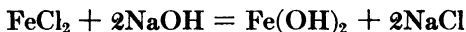
Its chlorine derivatives are the most important.

1. *Ferrous Chloride*, FeCl_2 , formed when metallic iron is dissolved in hydrochloric acid, is a white substance which deliquesces in moist air. It is very readily oxidized to ferric chloride;



2. *Ferric Chloride* is a yellow solid which decomposes into basic salts.

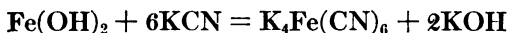
425. Hydroxyl Derivatives.—When the chlorides of iron in solution are made alkaline by the addition of an alkali hydroxide, the corresponding iron hydroxide is precipitated;



1. *Ferrous Hydroxide*, Fe(OH)_2 , is a white solid which quickly turns green, and finally brown, on exposure to the air. This is due to its oxidation to ferric hydroxide.

2. *Ferric Hydroxide*, Fe(OH)_3 , is precipitated as a voluminous, brick-red precipitate, which is permanent in the air.

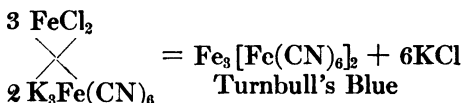
426. Cyanogen Derivatives. — Freshly precipitated ferrous hydroxide is dissolved by a solution of potassium cyanide, with the formation of potassium ferrocyanide, $\text{K}_4\text{Fe(CN)}_6$. The reaction may be expressed by the graph,



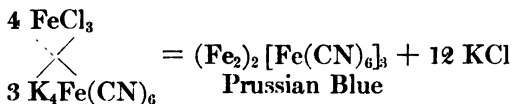
1. *Potassium Ferrocyanide* is a yellow, crystalline salt in which the iron is acting in combination with cyanogen as a compound negative radical, Fe(CN)_6 .

2. *Potassium Ferricyanide*, $\text{K}_3\text{Fe(CN)}_6$ (formed by treating the ferrocyanide, either dry or in solution, with chlorine gas), crystallizes in dark-red, monoclinic prisms.

A curious relation obtains between basic iron and its cyanogen derivatives. Thus, when ferrous chloride in solution is treated with potassium ferricyanide, a beautiful blue precipitate, called "Turnbull's Blue," is formed;



Ferric chloride in solution is decomposed by potassium ferrocyanide, forming "Prussian Blue";



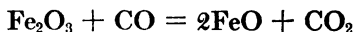
427. Oxygen Derivatives.—Iron combines with oxygen in three proportions:

FeO , ferrous oxide

Fe_2O_3 , ferric oxide

Fe_3O_4 , ferrous-ferric oxide

1. *Ferrous Oxide*, FeO , has not been prepared in a chemically pure form because of its great affinity for oxygen. A fairly pure product may be obtained by passing carbon monoxide over hot ferric oxide;



It is a black, glossy powder which dissolves in muriatic or sulphuric acid, forming the corresponding ferrous salt.

2. *Ferric Oxide*, Fe_2O_3 , found in great abundance in nature, is the chief ore from which iron is obtained (p. 113), and is always formed when iron is oxidized in the air. It is also a by-product in many industrial processes. It is extensively used in the manufacture of a red paint, and as a polishing material for glass, jewelry, brassware, etc. Ferric oxide is insoluble in water, and practically insoluble in acids. It is the base from which the ferric salts are derived.

Iron rust is a complex compound whose chief constituent is hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$).

3. *Ferrous-ferric Oxide*, Fe_3O_4 , occurs in black octahedral crystals which are magnetic, hence the name "loadstone." It is formed when iron is burned in an excess of oxygen, and when steam is passed over red-hot iron. It is widespread in

nature as an accessory mineral in certain sorts of igneous rock. It occasionally occurs in beds which are pure enough to constitute ore.

428. Salts of Iron.—It has already been pointed out that iron forms ferrous and ferric derivatives. Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the “green vitriol” or “copperas” of commerce, is formed when iron is dissolved in dilute sulphuric acid. It crystallizes in clear light-green crystals, and is extensively used as a mordant, disinfectant, and pigment.

429. Sulphur Derivatives.—Iron combines with sulphur in two proportions;

FeS , ferrous sulphide

FeS_2 , ferric sulphide

1. *Ferrous Sulphide*, FeS , made by fusing a mixture of iron and sulphur, is a yellow crystalline solid; but the commercial product is a blue-black crystalline substance which possesses a strong metallic luster. It is insoluble in water, but dissolves readily in dilute sulphuric or muriatic acid, liberating hydrogen sulphide (p. 29).

2. *Ferric Sulphide*, FeS_2 (iron pyrites), found in large deposits in nature, is a lustrous, brass-yellow solid, sometimes mistaken for gold, hence the common name “fool’s” gold. It is used in enormous quantities in the manufacture of sulphuric acid (p. 209). It is a common associate of metallic ores.

NICKEL, Ni (AT. WT. 58.7)

430. Occurrence and Properties.—This element, discovered by Cronstedt in 1751, is not found free in nature, but in combination with arsenic, copper, and sulphur. It is a white, lustrous metal, hard enough to take a high polish. It is readily soluble in hydrochloric and sulphuric acid, with the forma-

tion of the corresponding nickelous salts. It is not changed by moist air, and is, therefore, well adapted for plating and for the manufacture of alloys.

431. Alloys of Nickel.

TABLE LIV*

COMPOUNDS	NICKEL	COPPER	ZINC
German Silver.....	34....	46....	20....
German Silver.....	8....	58....	34....
German Silver.....	6....	63....	31....
Nickel Coins (U. S.).....	25....	75....	

Nickel steel, which contains about 4 per cent of nickel, is used extensively for armor-plate.

COMPOUNDS OF NICKEL

432. Nickel forms two series of compounds: the nickelous and the nickelic. The nickelous compounds are the most important.

433. Halogen Derivatives.—Nickel dichloride, NiCl_2 , forms small apple-green crystals which dissolve readily in water.

434. Oxygen Derivatives.—There are two oxides;

NiO , nickelous oxide

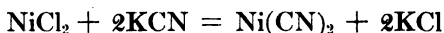
Ni_2O_3 , nickelic oxide

Nickelous Oxide, NiO , is a gray powder, and nickelic oxide, Ni_2O_3 , is black. Each is insoluble in water and each yields an hydroxide. Nickelous Hydroxide, $\text{Ni}(\text{OH})_2$, is an

* Data from Hiorns.

apple-green solid, and the nickelic hydroxide, $\text{Ni}_2(\text{OH})_6$, is black. Each of these acts as a base.

435. Cyanogen Derivatives.—When a neutral solution of nickel chloride is treated with a small amount of potassium cyanide, greenish-white nickel cyanide is precipitated;



An excess of potassium cyanide dissolves the precipitate, forming potassium nickel cyanide;



COBALT, Co (At. Wt. 59)

436. Properties of Cobalt.—Cobalt, which is always found associated with nickel, is a white, lustrous metal which is highly ductile, and takes a polish superior to that of nickel.

COMPOUNDS OF COBALT

437. Cobalt forms two series of derivatives: the cobaltous and the cobaltic. The cobaltous compounds are those generally met with.

438. Halogen Derivatives.—Cobaltous Chloride, CoCl_2 , is the most important salt of this series.

439. Oxygen Derivatives.—There are three oxides;

CoO , cobaltous oxide

Co_2O_3 , cobaltic oxide

Co_3O_4 , cobaltous-cobaltic oxide

Two of these oxides are basic: cobaltous oxide yields cobaltous hydroxide, $\text{Co}(\text{OH})_2$, and cobaltic oxide yields cobaltic hydroxide, $\text{Co}_2(\text{OH})_6$. These hydroxides dissolve in mineral

acids forming the corresponding salts. The chemical properties of cobaltous-cobaltic oxide are similar to those of ferrous-ferric oxide.

440. Cyanogen Derivatives.—Potassium cyanide precipitates cobaltous cyanide, $\text{Co}(\text{CN})_2$, from a solution of cobaltous chloride. It dissolves in an excess of the reagent, forming potassium cobalt cyanide, $\text{K}_4\overline{\text{Co}(\text{CN})_6}^+$

441. Other Compounds.—Certain silicates of cobalt have been used since the remotest times for coloring glass. When a mixture of cobalt ore, quartz sand, and potassium carbonate is fused, the product is an intensely blue, glass-like substance, known as "smalt." It is used extensively in decorating porcelain, and as a pigment. The cobalt pigments are the only compounds of cobalt which have commercial importance. They are not changed by acids or alkalis, or by sunlight or moisture.

THE IRON FAMILY

442. The similarity of these elements in their chemical relations, though not so pronounced as in some of the preceding groups, has led to their being placed in a natural family. A general view of these relations is given in the following table:

TABLE LV

	IRON ;	NICKEL	COBALT
Atomic Weight.....	55.9.....	58.7.....	59.0
Specific Gravity.....	7.84.....	9.0.....	8.5-8.7
Oxides.....	FeO ; Fe_2O_3 ; Fe_3O_4 ..	NiO ; Ni_2O_3 ...	CoO ; Co_2O_3 ; Co_3O_4
Sulphides.....	FeS ; FeS_2	NiS	CoS ; CoS_2
Cyanogens.....	$\text{Fe}(\text{CN})_2$; $\text{K}_4\text{Fe}(\text{CN})_6$; $\text{K}_3\text{Fe}(\text{CN})_6$	$\text{Ni}(\text{CN})_2$; $\text{K}_2\text{Ni}(\text{CN})_4$	$\text{Co}(\text{CN})_2$; $\text{K}_4\text{Co}(\text{CN})_6$; $\text{K}_3\text{Co}(\text{CN})_6$

CHAPTER XXIII

CLASSIFICATION OF ELEMENTS

443. Metals, Non-Metals, and Metalloids.—In Part II it has been shown that the groups of elements are fundamentally related. Thus the oxides of the *non-metals* phosphorus, arsenic, sulphur, carbon, etc., give rise to the common acids, while the oxides of the *metals*, sodium, potassium, barium, calcium, etc., are the common bases. Aluminium, chromium, zinc, antimony, and tin resemble metals, but their oxides act as acid anhydrides and assume, therefore, electrically negative attributes. Elements of this type were called *metalloids*. This classification of the elements into non-metals, metalloids, and metals is convenient, though the lines are not sharply drawn between the three classes. This classification was made during the early development of chemistry, when comparatively few elements were known. It soon led to confusion, because elements were discovered which did not fall clearly in any of these groups. A new plan of classifying the elements became necessary, and vigorous efforts were made to this end soon after Dalton announced his theory of multiple proportions. These efforts led to some interesting developments. Thus, Proust promulgated the theory that the atomic weights of all elements are exact multiples of the atomic weight of hydrogen, and that the atoms of other elements are merely aggregations of hydrogen atoms. This theory was so revolutionary that it aroused much discussion. The researches of Berzelius, Marignac, and Stas proved that Proust's hypothesis that the atomic weights of other elements are multiples of the atomic weight of hydrogen, was untenable. The atomic weights of the elements are not exact multiples of the atomic weight of hydrogen (p. 417).

Between 1828 and 1864 Dumas, Gladstone, Cooke, Newlands, and others attempted to arrange a number of the elements in the order of their atomic weights, and they pointed out that certain numerical relations exist between them. Thus, the atomic weight of selenium (p. 212) is one-half the sum of the atomic weights of sulphur (p. 204) and tellurium (p. 214). A like relation obtains between lithium, sodium, and potassium in Group VIII (p. 359), and phosphorus, arsenic, and antimony in Group III (p. 219).

$$S = 32, Se = 79.2, Te = 127.6; \frac{32 + 127.6}{2} = 79.8$$

$$Li = 7.03, Na = 23.05, K = 39.15; \frac{7.03 + 39.15}{2} = 23.09$$

$$P = 31, As = 75, Sb = 120.2; \frac{31 + 120.2}{2} = 75.6$$

444. The "Law of Octaves."—In 1864 Newlands showed that the elements could be arranged, according to their atomic weights, into groups of seven each, and that the gradation in properties of the elements in one group, were to some extent repeated in the next. This variation may be seen, for certain groups, in Table LVI. It contains elements* which have not been discussed in the preceding chapters, because many of them possess only theoretical interest.

TABLE LVI

I	II	III	IV	V	VI
AT. WT.	AT. WT.	AT. WT.	AT. WT.	AT. WT.	AT. WT.
F = 19.00	Cl = 35.45	Mn = 55.00	Br = 79.96		I = 126.85
O = 16.00	S = 32.06	Cr = 52.10	Se = 79.20	Mo = 96.0	Te = 127.6
N = 14.04	P = 31.00	V = 51.20	As = 75.00	Nb = 94.0	Sb = 120.2
C = 12.00	Si = 28.40	Ti = 48.10	Ge = 72.50	Zr = 90.6	Sn = 119.0
B = 11.00	Al = 27.10	Sc = 44.10	Ga = 70.00	Yt = 89.0	In = 114.0
Be = 9.10	Mg = 24.36	Ca = 40.10	Zn = 65.40	Sr = 87.6	Cd = 112.4
Li = 7.03	Na = 23.05	K = 39.15	Cu = 63.60	Rb = 85.4	Ag = 107.93

* For a list of the names and symbols of elements not given in the descriptive text, see Appendix, p. 417.

Now the basic properties of the elements in column I decrease uniformly with increase in the atomic weight until they reach a minimum in fluorine. The next element in the order of its atomic weight is sodium, which is again a strong base, and it is also the *eighth* element below lithium in the table. The same relation is found in the change in properties of the elements between sodium and chlorine, while potassium, the eighth element below sodium in the table, is again strongly basic. This relation may be noted in the succeeding columns. These facts led Newlands to affirm that the properties of every eighth element are necessarily a repetition of the attributes of the first, like the eighth note of an octave in music.

1st octave A B C D E F G

2d octave a b c d e f g

For this reason he called this behavior the "law of octaves." Table LVI shows clearly that there is a *periodic variation* in the properties of the first twenty-one elements beginning with lithium, when they are arranged in the order of their atomic weights. This rhythmical variation is the basis of the "periodic law."

445. The Periodic Law.—Until 1869 Newlands' "law of octaves" was the broadest basis for the classification of the elements. In that year Mendelejeff, a Russian chemist, published his classification of the elements according to the periodic law. His scheme was broader, and included more elements than Newlands' law of octaves. Lothar Meyer, a German chemist, made other contributions to Mendelejeff's scheme. Meyer stated the law thus: "If the elements are arranged in the order of increasing atomic weights, the properties of these elements vary from number to number of the series, but return more or less nearly to the same values at certain fixed points in the series." The present method of arranging the elements according to the periodic law is shown in Table LVII.

TABLE LVII*

PERIOD	GROUP I R_2O	GROUP II R_2O_2	GROUP III R_2O_3	GROUP IV R_2O_4	GROUP V R_2O_5	GROUP VI R_2O_6	GROUP VII R_2O_7	GROUP VIII R_2O_8
1	Li = 7.03 †	Be = 9.1	B = 11.0	C = 12.0	N = 14.04	O = 16	F = 19	
2	Na = 23.05	Mg = 24.36	Al = 27.1	Si = 28.4	P = 31.0	S = 32.06	Cl = 35.45	
3	K = 39.15	Ca = 40	Sc = 44.1	Ti = 48.1	V = 51.2	Cr = 52.1	Mn = 55	[Fe = 56 Co = 59 Ni = 58.7]
4	Cu = 63.6	Zn = 65.4	Ga = 70	Ge = 72.5	As = 75.0	Se = 79.2	Br = 79.96	[Ru = 101.7 Rh = 103.0 Pt = 106.5]
5	Rb = 85.4	Sr = 87.6	Yt = 89	Zr = 90.6	Nb = 94	Mo = 96.0		
6	Ag = 107.93	Cd = 112.4	In = 114.1	Sn = 119.0	Sb = 120.2	Te = 127.6	I = 126.8	[Os = 191 Ir = 193 Pt = 194.8]
7	Cs = 133	Ba = 137.4	La = 138.9	Ce = 140	Pr = 140.5	Nd = 143.6		
8								
9			Er = 166		Ta = 183	W = 184		
10	Au = 197.2	Hg = 200	Tl = 204.1	Pb = 206.9	Bi = 208.5			
11				Th = 232.5		V = 238.5		

* For the meaning of unfamiliar symbols, see App. p. 417. † International Atomic Weights; O = 16.

Three important points concerning the interpretation of Table LVII must be noted:

(1) It includes more elements than have been studied in the descriptive text.

(2) The *vertical* columns in Table XLIX have been made the *horizontal* columns in Table LVII. It will be readily seen that this does not in any degree alter the periodic variation.

(3) The groups (vertical columns) are numbered in *reverse* order to those used in the descriptive text, but the elements of each group are the same. Thus, in Table XLIX, Group I (reading from left to right) contains F, Cl, Br, I, while in Table LVII, Group VII (reading from top to bottom) contains the same elements. The *customary* method of numbering and arranging the groups is that given in Table LVII. The opposite order was adopted in the descriptive text, because the halogens were so closely related to the material in Part I that their further study required immediate attention. The other groups were arranged in succession for the same reasons.

446. The Gaps in the Periods.—In Table LVII the natural families or groups are put in the vertical columns, and the “periods” of variation are in the horizontal rows. A blank in the table means that no element whose atomic weight would put it in that place, is known. Thus, in the fifth period there is no element known whose atomic weight places it in Group VII. The next element after molybdenum ($\text{Mo} = 96$) in the order of increasing atomic weight is ruthenium ($\text{Ru} = 101.7$).

Now if this element were placed under manganese, as its atomic weight suggests, it would require a rearrangement of all the elements which follow it, because its chemical attributes place it clearly in Group VIII. Hence, a vacant space is left, believing that an element whose atomic weight is approximately 100 and whose attributes are related to manganese, may yet be discovered.

This faith in the existence of undiscovered elements is not without some foundation. Mendelejeff predicted the properties and the principal compounds of elements then unknown. Thus, gallium ($\text{Ga} = 70$) in Group III, Table LVII, was not

discovered till 1875. Mendelejeff predicted an element whose atomic weight would be about 69, its specific gravity, 5.9, etc. Gallium corresponds to his hypothetical element.*

MENDELEJEFF'S PREDICTION	GALLIUM
Atomic Weight about 69.....	Atomic Weight = 70
Readily obtained by reduction.	Readily obtained by electrolysis
Low melting point	Melting point = 30°
Specific Gravity 5.9.....	Specific Gravity = 5.93
Slowly attacked by acids.....	Soluble in hot hydrochloric acid
Soluble in alkalis	Dissolves in caustic potash

Two other elements, scandium and germanium, corresponding to those whose existence he also predicted, have since been discovered. The verification of these predictions is striking evidence that the "periodic law" is a real law of nature. This law may be stated thus: *The properties of the elements are periodic functions of their atomic weights.*

447. Uses of the Periodic Law.—This law is of great service to the investigator in determining the atomic weight, specific gravity, melting point, and other physical properties of an element.

Thus, suppose it is found that sodium chloride is 39.4 per cent sodium and 60.6 per cent chlorine. Is the formula NaCl or some multiple thereof? Does sodium combine with an atomic weight of 23, or 23×2 ? It was pointed out on page 185 that the specific depression of the freezing point for salt is about twice too high. This, it was explained, is due to ionization. Suppose we take the opposite view and affirm that the molecular weight of NaCl is 117, and that the atomic weight of sodium is 46. Then its place in the periodic system would be immediately after scandium in the third period, and below silicon in Group IV. Its chemical properties ought to be essentially those of a non-metal, whose oxide is a weak acid anhydride.

But it is well known that this is *not* the case. It is a metal whose oxide is a very strong base. These attributes would place it in the

* See Muir: Principles of Chemistry.

first group. Evidently the contradiction is to be referred to the *assumed* molecular weight, 46, for sodium takes its true place in the period, as determined by its chemical properties, when its atomic weight is assumed to be 23.

The law is of great service as a control over results which have been obtained by diverse methods. It has led to a more accurate determination of the atomic weights of certain elements. It enables the student to anticipate the essential properties of an element with which he is experimentally unacquainted. Suppose it is desired to ascertain the fundamental attributes of molybdenum ($M\phi = 96$). Reference to Table LVII shows that it follows chromium. Now chromium (p 330) forms three oxides: CrO , Cr_2O_3 , and CrO_3 . The first two are basic, but the third is a strong acid anhydride. Molybdenum forms four oxygen derivatives: MoO , Mo_2O_3 , MoO_2 , and MoO_3 . The first three are bases but the fourth is the anhydride of molybdic acid, H_2MoO_4 . The similarity of the two elements may be seen in the following table.

TABLE LVIII

DERIVATIVES	CHROMIUM	MOLYBDENUM
Oxides	CrO ; Cr_2O_3 ; CrO_3	MoO ; Mo_2O_3 ; MoO_2 ; MoO_3
Chlorides	CrCl_2 ; Cr_2Cl_6	MoCl_2 ; MoCl_3 ; MoCl_4 ; MoCl_5
Other Compounds	K_2CrO_4 ; PbCrO_4 , etc.	K_2MoO_4 ; PbMoO_4 , etc.

CHAPTER XXIV

CHEMISTRY AND LIFE

448. Elements Necessary to Plant Life.—The compounds of less than twenty elements are found in abundance in the soil. The most important of these, arranged in the order of their abundance, are the compounds of oxygen, silicon, aluminium, iron, calcium, magnesium, sodium, potassium, titanium, hydrogen, carbon, phosphorus, manganese, sulphur, chlorine, nitrogen, barium. Ten of these elements are necessary to the normal growth of green plants,* but phosphorus, carbon, and nitrogen are essential to their life. During plant growth the chlorophyll changes carbon dioxide, which is a strong exothermic compound (97 Cal.), into starch, and in so doing it stores up energy. Thus, under favorable conditions, the green tissue of the ordinary sunflower builds up about 2.5 gm. of starch per square meter of leaf surface every fifteen hours during clear August weather, and in so doing stores about 100.4 calories of heat. The plant must be supplied abundantly with carbon dioxide in order to perform this function.

Of the other elements essential to plant growth, nitrogen is one of the most important, but it must exist in the soil as a soluble nitrate, e.g., potassium nitrate, in order to be taken by the rootlets of the plant and transformed into albumen within the plant substance. The supply of soluble nitrates to the soil is, therefore, one of the most important problems of the agriculturist, and their production from other nitrogenous materials has commanded the attention of many scientists.

* Strasburger: *Lehrbuch der Botanik*, page 168.

449. Sources of Nitrogen.—There are three sources from which nitrogen is supplied to plants: nitrate beds, complex nitrogenous substances, and the air.

I. Nitrate beds are mainly Chili saltpeter, NaNO_3 . These are mined and the saltpeter is applied to the soil either alone or mixed with bone meal.

II. Organic nitrogenous substances occur as vegetable or animal albumen, urea, humus, etc. When a plant or an animal dies, the albumen and other nitrogenous compounds which its body contains are transformed into soluble nitrates. There are three fundamental stages in the process: (A) the formation of ammonia, (B) the oxidation of ammonia to nitrites, and (C) the oxidation of nitrites to nitrates.*

A. *Formation of Ammonia.*—A piece of decaying lean meat gives off ammonia. When fresh meat is canned, it may be kept for many months at ordinary temperatures without change; but if it is again exposed to the air, decomposition will occur. These facts indicate that the active agent in the decay is present in the air. This agent has been found to be certain exceedingly minute plants called *bacteria*. These bacteria feed upon the nitrogenous material and produce ammonia, but cannot oxidize the ammonia to a nitrate. Marchal has isolated and studied some of the ammonia-making bacteria, the most active of which he called *bacillus mycoides*. The most important facts about its activity are these: (1) When it grows upon albumen, ammonium carbonate is always formed; (2) the organic carbon is changed chiefly to carbon dioxide; (3) the sulphur is transformed into hydrogen sulphide; (4) no nitrogen or hydrogen is set free; and (5) it does not act in a pure salt of ammonium or a nitrate (Wiley).

B. *Oxidation of Ammonia.*—The ammonia is oxidized to nitrous acid or a nitrite by other bacteria, namely a species called *nitrosomonas* (Fig. 82).

*Strasburger: Lehrbuch der Botanik, page 178.

C. A third species, which the discoverer named *Nitrobacter* (Fig. 83), oxidize the nitrites to nitrates. The chemical

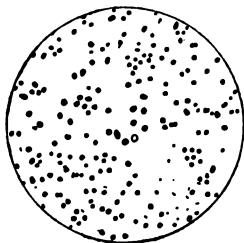


FIGURE 82

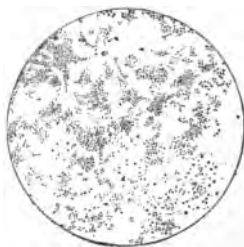
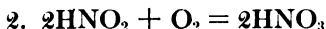
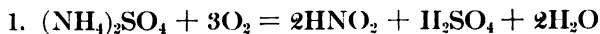
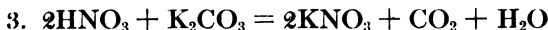


FIGURE 83

changes in oxidizing ammonia to nitric acid may be expressed by the graphs;



The free nitric acid is immediately neutralized by the carbonates in the soil;



Therefore, we may conclude that nature converts the nitrogenous compounds, which are of no further use to animals or plants, into inorganic nitrates through the activity of three kinds of bacteria: (1) the ammonia producers, (2) the nitrifying germs, and (3) those which eventually form nitrates.

III. *Fixation of Free Nitrogen*.—It has been discovered that the roots of certain leguminous plants develop nodules upon their surfaces. The roots of the common clover, Fig. 84, are also knotted. These nodules are found to be made up of coarse granular cells which contain active bacteria. That the bacteria fix the nitrogen of the air is shown by two experiments:

(a) If a quantity of soil of known composition is heated to from 150° to 200° * for some hours and then sown with clover and the crop when grown is not removed but plowed under, analysis of the soil will show that its nitrogen has not been increased.

* Most species of bacteria are killed at this temperature.

(b) If the same quantity of seed is sown in the same amount of soil not sterilized by heating, there will be a larger crop, and the total quantity of nitrogen in the soil will be materially increased.

The inference is that the germs within the nodules on the rootlets either absorb and transform the free nitrogen from the air into plant food, or they stimulate the plant to do so.

The fixation of atmospheric nitrogen is very important, for during the combustion of nitrogenous substances the nitrogen is set free because of its chemical indifference. Its loss to the plant and animal world through combustion is prevented by oxidation due to the activity of bacteria.



FIGURE 84

450. The Rotation of Nitrogen.—Let us suppose that potassium nitrate is fed to growing corn. The rootlets of the corn absorb it and within the plant it becomes vegetable albumen, which is strongly endothermic. The vegetable albumen is consumed by cattle, digested and assimilated into animal albumen (lean meat). A piece of lean meat is, therefore, a store-house of potential energy. Suppose one pound of it lies in the air and another pound is consumed by some animal. The first pound will be at once attacked by bacteria, and the organic nitrogen will be changed to ammonia. During this process the potential energy will be dissipated as heat. The ammonia will then be oxidized to nitrites and nitrates by the nitrifying and nitroifying bacteria, in which condition it may be absorbed by the growing plant.

The second pound is slowly oxidized in the tissues of the animal which ate it. Much of the carbon is oxidized to carbon dioxide, much of the nitrogen is transformed into urea, $\text{NH}_2\text{CO.NH}_2$, and both are excreted. The urea is quickly changed to ammonium carbonate, and this in turn will be oxidized to nitrites and ultimately to nitrates by the processes which have been outlined.

During this oxidation of the albumen to urea within the tissues of the animal, the potential energy of the albumen is transformed into animal heat, muscular power, and perhaps mental activity. It is estimated that about four-fifths of the energy of food is changed to heat in maintaining the body temperature. This heat is slowly radiated into space. The remaining one-fifth becomes muscular force; but this force is also finally changed to heat. It thus appears that animal life is maintained by dissipating energy. The living organism, therefore, owes its immediate activity to the fact that the normal course of spontaneous chemical action is toward the formation of those compounds which are strongly exothermic. But how does nature compensate for this loss of energy? Through photosynthesis. Since energy cannot be created, and since the products of photosynthesis are endothermic compounds, it follows that the loss in radiation through oxidation is made good by the energy which comes from the sun. Hence, the sun is the source of earth power, and the cycle of life is intimately bound up with the formation of endothermic compounds and their subsequent oxidation to exothermic ones. It is not strange that our ancestors looked to the sun as the source of all good, and that each day they knelt with faces toward the east, and with the first glimpse of the dawn prayed, "Thou who art a blessing where thou art, drive away the unfriendly; make the pastures green; give us safety; remove our enemies; bring treasures; raise wealth to thy worshipers, Thou Mighty Dawn."

APPENDIX

The following pages contain brief descriptions of some fundamental pieces of apparatus, and some suggestions as to the best methods of manipulating them.

451. Thermometer.—The thermometer used in scientific experiments is the centigrade or Celsius thermometer. The freezing point of pure water by this instrument is 0° , and its boiling point is 100° . The thermometer in popular use in this country is the Fahrenheit. On this instrument the freezing point of water is 32° , and the boiling point is 212° .

The temperature centigrade may be changed to temperature Fahrenheit, and vice versa, by the solution of the following equations:

$$C^{\circ} = \frac{5}{9} (F^{\circ} - 32)$$

$$F^{\circ} = \frac{9}{5} C^{\circ} + 32$$

452. A Water-Bath is used for heating when the temperature is not to exceed 100° . When the bath is used for evaporating, the dish or other vessel is placed upon the proper ring and the water in the bath is kept boiling. A good water-bath is shown in Fig. 85.

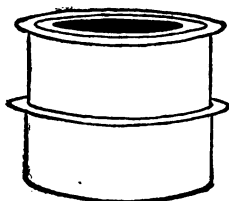


FIGURE 85

453. Drying Oven.—A very serviceable form of oven for drying objects at 100° is shown in Fig. 86. It consists of

a double-walled box which is made of copper or galvanized iron. The space between the walls may be filled with water from the opening at W. When heat is applied from below, the water between the walls boils, and thus maintains the temperature of the interior at 100° .

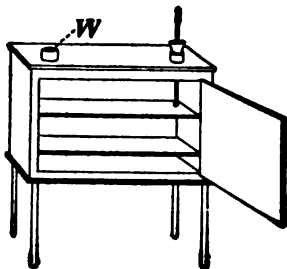


FIGURE 86

454. Pneumatic Trough.—

This piece of apparatus is ordinarily made of sheet or galvanized iron and afterwards coated with japan or enamel paint. It is usually provided with an adjustable stage S (Fig. 87), which has a number of openings through which tubes may be passed. These troughs are serviceable in collecting gases. The trough is filled with water until it rises to a depth of at least 2 cm. over the stage. The receiver is filled with water, and its mouth is covered with a glass

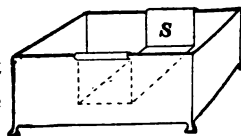


FIGURE 87

plate. It is then inverted in the water and rested on the stage. The point of the delivery tube which conveys the gas to the receiver is thrust up through an opening, into the mouth of the receiver.

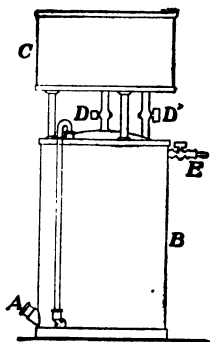


FIGURE 88

455. A Gasometer.—A convenient form of gasometer is shown in Fig. 88. The reservoir B is filled with water by opening the cocks D D' E, and pouring water into C until it flows out at E. The cocks are then closed, the stopper A removed, and

the tube carrying the gas to be collected is thrust up into the receiver B at A. As the gas collects in B, an equivalent

volume of water is expelled from A. When a sufficient quantity of gas is obtained, the tube is removed from A and the stopper securely set. To draw off the gas from B, fill the reservoir C with water and open the cocks D D' and E. The water runs through the cocks D D' into B and forces the gas out through E.

456. Measuring Liquids.—For scientific experiments the metric system of volumes and weights is used almost exclusively. The unit of volume is the cubic centimeter, and the unit of weight is the gram. One cc. of pure water at 4° weighs 1 gm. One gm. = 0.035 oz. = 15.4 gr.

In measuring liquids there are three pieces of apparatus which are especially serviceable:

I. A *graduated flask* is shown in Fig. 89. The capacity of the flask, when filled to the ring cut in the neck, is marked in cc. upon the side. Thus, the flask shown in Fig. 89 contains 500 cc. when it is filled to the mark A.

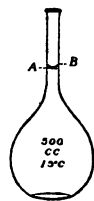


FIGURE 89

In the neck of the flask the liquid climbs higher upon the sides than it does in the center. The surface of the liquid is therefore concave. Thus, in Fig. 89 the edges reach to B, while the base of the crescent coincides with the mark A. The concave curve is called the *meniscus*. In measuring, hold the flask so that A is on a level with the eyes, and fill until the bottom of the meniscus exactly coincides with A.

II. A *pipette* is shown in Fig. 90. It is a piece of glass tubing expanded in the middle to increase its capacity. A graduating mark A is cut into the upper shaft, and the volume of the pipette from this mark to the point is marked, on the enlarged portion of the tube. In using a pipette, insert the point into the liquid which is to be measured, and suck on the upper end of the tube until the liquid is forced past the

graduating mark. Quickly close the opening at B (Fig. 90) with the forefinger, and then allow the liquid to run out until the bottom of the meniscus coincides with the mark A. The pipette will then contain a specific quantity of liquid, in this illustration, 20 cc.



FIGURE 90

III. *The Burette.*—A burette (Fig. 91) is graduated usually to tenths of a cubic centimeter, and reads from the top.

The tube is filled to a height above the zero mark, and then the liquid is allowed to run out by adjusting the cock M until the bottom of the meniscus coincides with the zero mark. The liquid drawn out is measured by the fall of the meniscus, read upon the graduated scale.

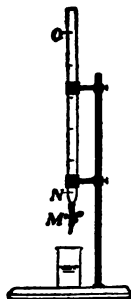


FIGURE 91

457. Weighing Solids.—A pair of balances for weighing accurately a small quantity of substance is shown in Fig. 92.

Process.—Place the object to be weighed (its weight should not exceed 50 gm.) in the pan B, put a weight of about the same mass in the pan B', and turn the eccentric A until the needle E swings to the right or left. If it swings to the right, the object is heavier than the weight in B'; if to the left, it is lighter. Suppose it is heavier than the weight. Turn the eccentric A until the needle comes to rest, add a small weight to the one in B', and again swing the needle as above directed. Continue the trials, each time adding successively smaller weights, until the smallest weight in the set, e.g., 0.01 gm. causes the needle

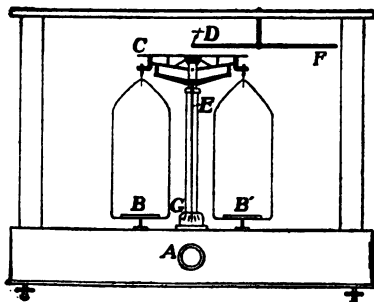


FIGURE 92

to swing to the left, and is therefore too heavy. Remove this weight and place the rider D on the beam C to the right of the middle point. This beam is usually divided into two equal parts by a zero mark at the center, and each half is divided into 10 equal parts. Each

of these parts represents 0.1 of 0.01 gm. or .001 gm. In some balances each of these 10 parts is again divided into 10 other parts, each of which represents 0.1 of .001, or .0001 gm. Adjust the rider by the arm F until a point is found at which the needle, when it is left free to swing by turning the eccentric A, will swing to equal distances on each side of the zero mark on the dial G. The sum of the weights in the pan B' plus the weight indicated by the rider are equivalent to the weight of the object.

Example.—Suppose the weights in the pan are 20 gm., 0.1 gm., 0.02 gm., and the rider is at 6 on the beam (indicating .006 gm. additional weight); then the object weighs 20.126 gm.

In weighing, a weight should never be placed in the pan B', or the rider adjusted on the beam, until the needle is brought to rest by the eccentric A, otherwise the balances will be thrown out of adjustment.

458. Hydrogen Sulphide or Hydrogen Generator.—

A convenient form of this very useful piece of apparatus is shown in Fig. 93. It consists of a large glass cylinder A, which is provided with a wooden stopper which has fitted into it a second and much smaller cylinder B. The inner cylinder B is also equipped with a good stopper C, through which is passed a glass tube carrying a stopcock D, and arranged as shown in the cut.

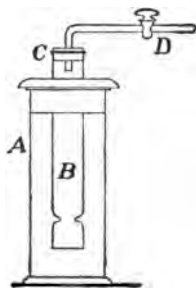


FIGURE 93

a. For generating hydrogen sulphide, the cylinder B is filled with lumps of iron sulphide about the size of a small peanut. The large cylinder is filled to three-fourths of its capacity with commercial sulphuric acid (1:4) and the inner cylinder is placed in position. When the cock D is open, the acid rises up into the inner cylinder and acts upon the iron sulphide, generating hydrogen sulphide. When the cock D is closed, the gas which accumulates in B pushes the acid out into the larger cylinder, and thus the chemical action ceases until the gas is again drawn off.

b. For generating hydrogen, granulated zinc is substituted for iron sulphide, otherwise the process is the same. Sometimes hydrochloric acid is substituted for the sulphuric acid because the action is more energetic.

459. Glass Tubes.—I. To Cut Glass Tubes.—If the tube has a narrow diameter, it may be cut by making a slight scratch upon it with the edge of a three-cornered file, and then breaking it by holding one end of the tube in each hand, and pulling downward and outward.

A tube of large diameter is more difficult to cut. It may be cut successfully in the following way: Scratch a complete circumference upon it with a three-cornered file, and then make the scratch about 1 mm. deep with the file, which should be frequently dipped into water. Now direct a blow-pipe flame against the cut circumference so that it shall strike the glass tube almost at a tangent. Usually the heat will cause the glass to break along the tracings of the file.

A cut piece of tubing should always have the edges rounded off. They may be smoothed by being either gradually heated in the apex of a bunsen flame, or by filing.

II. To Bend a Glass Tube.—Tubing cannot be bent successfully in the flame of a bunsen burner; it will collapse at the angle, as shown in Fig. 94. Such a bend is easily broken



FIGURE 94

and impedes the passage of gas. To bend a tube so that it shall have a uniform diameter at the bend, it must be softened in a flat flame, such as is shown in Fig. 95.

When a tube is to be bent into an angle, hold it in the flame until it is quite soft, and then gently bend it by bringing the hands together, taking care to keep the softened portion of the tube in the flame all the while.

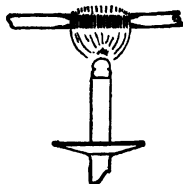


FIGURE 95

III. *To Draw a Glass Tube.*—Soften the tube in the colorless flame of a bunsen burner by holding it well into the upper part of the flame, and rotate it slowly so that it may be uniformly heated. Draw gently at first, then, when the glass stiffens, pull quickly and maintain the tension until it has become rigid. See Fig. 96.

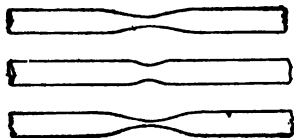


FIGURE 96

The most important point to observe is that the glass shall be kept constantly in the flame while it is being softened, otherwise it will not be uniformly heated, and this will cause it to draw irregularly.

IV. *To Set a Platinum Wire into a Glass Tube.*—Draw the tube out to a point as directed in III, break it off so that the opening will be just large enough to admit the point of the wire, insert the wire and then dip the point of the tube into the gas flame until it melts down and adheres to the wire. The position of the wire may be fixed as desired while the glass is still soft.

V. *To Seal a Glass Tube.*—Draw the tube to a point as directed in III, cut it off, and hold the point in the apex of the colorless flame until it closes up. This will give a point which is thick and likely to crack. This may be remedied by reheating the point until it softens, placing the open end between the lips and blowing with a gentle pressure until the collapsed walls expand, slowly rotating the glass at the time.

460. Cork Stoppers.—Select a stopper which is a little too large for the opening for which it is intended, dip it two or three times into hot water, and then compress it with a cork-squeezer or with the fingers until it fits the opening snugly.

The cork must then be bored to admit the glass tube

which is to pass through it. This is done most readily by a brass tube with a sharpened end (called a cork-borer).

The hole should be bored a little smaller than the tube, so that the tube may fit snugly. To bore the hole, place the base of the cork against the edge of the table, hold the cork firmly in position with the left hand, and with the right force the borer down the center with a motion like that of boring with a gimlet.

461. To Insert a Glass Tube Into Rubber Tubing.—Cut the rubber tubing at an acute angle, place the end of the glass tube in the cavity which is thus formed, and force the rubber over the glass until it adheres firmly.

462. Filtering.—The filter paper should be circular and of such a diameter that its radius is equal to about one-half the depth of the funnel. Fold the paper twice so that it

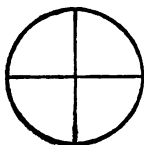


FIGURE 97



forms a quadrant, Fig. 97, and open it so that three layers of the paper will be on one side and one on the other. Place the paper in the funnel and wet it with distilled water so that it will adhere to the

sides. Pour the liquid to be filtered down the side of a glass rod. One end of the rod should touch the edge of the vessel from which the liquid is poured; the other end should touch the side of the filter, so that the liquid will not fall directly upon the apex of the paper.

463. Evaporating.—For evaporating a liquid at 100° , see page 403. For evaporating a liquid rapidly, place the dish containing the liquid on a wire gauze on an iron ring-stand, and bring the flame of the bunsen burner directly under it. To prevent breakage, a porcelain dish should be used.

464. Distilling.—Flask A (Fig. 98) is provided with a delivery tube B, which is connected with the inner tube C of the condenser D. The inner tube of the condenser is cooled by flowing water which comes in through the tube E and flows out through the tube F. The liquid to be distilled is put in A, and the distillate received from C.

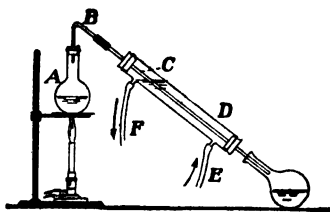


FIGURE 98

465. Fusion.—To fuse a substance, place it in a porcelain crucible of suitable size, cover with a lid, rest the crucible in an iron triangle, and heat it directly over the colorless flame of a bunsen burner or blast lamp. If the crucible contains too much it may be broken by the expansion of the material when it cools.

466. Preparation of Copper Oxide.—Dissolve about 20 gm. of copper nitrate in 100 cc. of *distilled water*, filter off any insoluble particles, evaporate the filtrate to dryness under the hood, and heat the dried residue in a porcelain or iron crucible until it is of a uniformly black color.

467. To Graduate a Glass Tube.—Place the tube (which should be closed securely at one end) firmly in an upright position, add 1 cc. (or any other desired quantity) of water from a burette, mark on the glass, by scratching it with a sharp file, the height to which the liquid extends, and repeat this after each additional cc. is added until the tube is graduated throughout its whole length.

468. To Prepare an Electromagnet.—A (Fig. 99) is a wide-mouthed jar of about 500 cc. capacity. E is a piece of dry oak or poplar wood 4 cm. wide and of a length somewhat greater than the diameter of the

jar. C and Z are plates 4 cm. wide and 15 cm. long, composed respectively of carbon and zinc. These are secured to the opposite sides of E

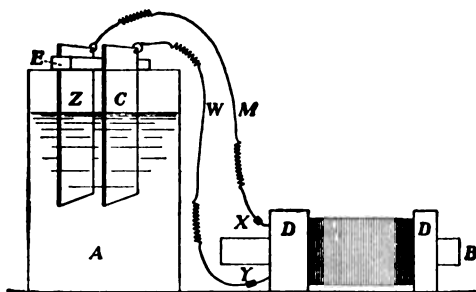


FIGURE 99

by screws, as shown in the cut. Each is fitted at the top with a binding post which serves to connect it with the wire W or M. D D is an ordinary spool which has wound on it 3-5 yds. of No. 24 insulated copper wire. B is a piece of iron bar fitted into the central opening of the spool. Its length should be somewhat greater

than that of the spool. The wires W and M may be connected by binding screws with the ends of the wire which surrounds the spool. Fill the jar with a potassium dichromate solution prepared according to the following proportions:

Water.....	1,000 gm.
Sulphuric Acid.....	400 gm.
Potassium Dichromate.....	130 gm.

Connect the apparatus as shown in the cut and touch the sample to be tested with B; if it is immediately attached it is said to be magnetic.

469. Quantitative Relation of Pressure to the Volume of a Gas.—The ratio of pressure to the volume of a gas may be ascertained as follows: A (Fig. 100) is a glass tube bent into a U-shape at the lower end. The length should be about 150 cm. It is provided with stopcocks at C and D for ingress and egress of gas. Suppose we wish to observe the influence of varying pressure on a volume of hydrogen. Pour clean, dry mercury into the funnel at E until it stands at the height B B'. Connect C with a hydrogen generator which is provided with a calcium chloride tube for drying the gas. Open the cock at D and allow the gas to pass until all air is expelled from the part C D. Close the cocks C and D. The pressure on the hydrogen B' D will be one atmosphere. Let B' D be a unit volume of gas,

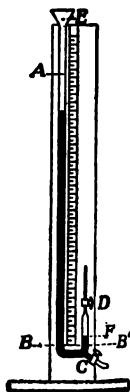


FIGURE 100

e.g., 10 cc.; then unit pressure (one atmosphere) yields unit volume. Expressed in an equation:

$$P : V :: 1 : 1$$

Measure accurately the height of B' D. Suppose it is 10 cm. Now pour in mercury at E until it stands at about 20 cm. above B. Measure the exact height from F to the top of the mercurial column and record results. Measure also the height of the hydrogen volume from the top of the mercury F to D. This will, of course, be somewhat less than B' D, for the gas is under increased pressure and must, therefore, have decreased in volume. Repeat the process with successive quantities of mercury until five or six readings shall have been made. Record results. The following readings were made by a student:

TABLE LIX

HEIGHT OF B' D = VOL. GAS	HEIGHT OF A- B = INCREASED PRESSURE	TOTAL PRESSURE IN ATMOS- PHERES	PRESSURE VOL- UME
1. 10 cm. = unit volume....	0.	1 atmosphere = 750 mm.	$1 \times 1 = 1$
2. 8 cm. = $\frac{8}{10}$ of unit vol....	19.4 mm.....	$1 + \frac{194}{750} = 1 \frac{194}{750}$	$1 \frac{194}{750} \times \frac{8}{10} = \frac{755}{750} +$
3. 7.1 cm. = $\frac{71}{100}$ of unit vol.	33.3 mm.....	$1 + \frac{333}{750} = 1 \frac{333}{750}$	$1 \frac{333}{750} \times \frac{71}{100} = \frac{768}{750} +$
4. 7.3 cm. = $\frac{73}{100}$ of unit vol.	288 mm.....	$1 + \frac{288}{750} = 1 \frac{288}{750}$	$1 \frac{288}{750} \times \frac{73}{100} = \frac{757}{750} +$
5. 6.0 cm. = $\frac{60}{100}$ of unit vol.	510 mm.....	$1 + \frac{510}{750} = 1 \frac{510}{750}$	$1 \frac{510}{750} \times \frac{60}{100} = \frac{756}{750} +$

It is to be observed from these results that the product of pressure and volume is in each case practically unity. This may be expressed by the equation, $P \times V = 1$. Otherwise stated, it means that the product of pressure and volume is always constant (p. 40). In order to maintain this product as a constant quantity, the pressure must decrease as the volume increases, or vice versa. The law is generally stated thus: The volume of a gas varies inversely as the pressure upon it. This is Boyle's law.

470. To Ascertain the Volume of a Gas at 0° Temperature.

Let v = volume at 0°

Let v' = observed volume

Let t = observed temperature

Then $273 + t : 273 :: v' : v$ (see page 41).

$$v \times (273 + t) = 273 v'$$

$$v' = \frac{v \times (273 + t)}{273} = \frac{273v}{273} + \frac{vt}{273} = v + \frac{vt}{273} = v + v \times \frac{t}{273}$$

$$\text{Now } \frac{t}{273} = t \times \frac{1}{273} = t \times 0.00366 = 0.00366t$$

Substituting we shall have,

$$v' = v + (.00366 \times t)v$$

$$v' = v \times (1 + .00366 \times t)$$

$$\therefore v = \frac{v'}{1 + .00366t}$$

471. To Ascertain the Volume of a Gas at 760 mm. Pressure.—The ratio of pressure to volume may be expressed by the proportion, $v : v' :: P' : P$, in which P' is the observed pressure, P is 760 mm. pressure, v is the volume at 760 mm., and v' is the observed volume. Then $v = \frac{v'P}{760}$.

472. To Ascertain the Volume of a Gas at 0° Temperature and 760 mm. Pressure.—The corrected volume for both temperature and pressure will be equivalent to the product of these two corrected values. To reduce a given volume of gas to that volume which would exist at 0° and 760 mm., it must be multiplied by $\frac{1}{1 + (.00366t)}$ and then by $\frac{P'}{760}$

Hence
$$v = v' \times \frac{1}{1 + (.00366t)} \times \frac{P'}{760}$$

$$v = \frac{v'P'}{760(1 + .00366t)}$$

473. To Prepare Starch Paste.—Triturate about 0.2 gm. of starch and 20 cc. of water in a mortar until they are thoroughly mixed. Pour this fluid into about 200 cc. of actively boiling water, and keep the mixture boiling for about five minutes.

474. Preparation of Sulphur Trioxide.—Put from 10 to 20 cc. of fuming sulphuric acid (also called Nordhausen acid) into a dry retort having a glass stopper, and connect it with a dry glass receiver which is surrounded by a mixture of ice and salt. Heat the retort carefully and collect the distillate in the cold receiver.

475. To Prepare a Solution of Oxalic Acid Containing 4.5 gm. in 1,000 cc. Water.—Pure oxalic acid contains two molecules of crystal water [$\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$]; hence, its molecular weight is 126, while that of the anhydrous acid is only 90; therefore it will be necessary to weigh out 6.3 gm. of the crystallized acid to obtain 4.5 gm. of the anhydrous acid, $\text{H}_2\text{C}_2\text{O}_4$. Pulverize and weigh accurately about 6 gm. of the crystallized acid. A convenient method of weighing such a quantity without loss is to put it into a small, clean, and thoroughly dried test-tube which is provided with a good stopper. Weigh the stoppered tube with its contents.

Now open the tube over the mouth of a large flask, which is also clean and dry, and let the powder drop into the flask, taking great care that none is lost. Some will adhere to the tube. Re-stopper the tube and weigh again. The loss in weight will give the exact amount of the acid in the flask.

Suppose the amount weighed out was 5.377 gm.; then the necessary amount of water to be added so that the solution will be equivalent to 4.5 gm. in 1,000 cc., may be determined

by the following proportion, in which X represents the amount of water needed:

$$6.3 : 1000 :: 5.377 : X; X = 853.5 \text{ cc.}$$

The chief reason for selecting oxalic acid is that it can be obtained pure and is easily handled without loss. The immediate purpose is to obtain an acid in solution whose strength is known. In this instance we shall have a proportion of 4.5 gm. of anhydrous acid, $\text{H}_2\text{C}_2\text{O}_4$, in 1,000 cc. of water.

476. To Prepare a Solution of Sodium Hydroxide Containing 4.0 gm. in 1000 cc. of Water.—Dissolve about 5 gm. of sodium hydroxide in approximately 900 cc. of distilled water, mix well, fill a burette with the solution and titrate it (p. 160) against the oxalic acid solution which contains 6.3 gm. of acid in 1,000 cc. of water, using phenolphthalein or litmus to determine the neutral point. Suppose 10 cc. of acid required 8.5 cc. of hydroxide to neutralize it. By adding 1.5 cc. of water to 8.5 cc. of the sodium hydroxide solution, its volume will be increased to 10 cc., i.e., the acid and alkali will be of the same strength. Suppose it is desirable to dilute 500 cc. of the sodium hydroxide solution to the same extent. The following proportion will obtain:

$$8.5 : 1.5 :: 500 : X; X = 88.2 \text{ cc.}$$

the amount of water to be added to 500 cc. of the sodium hydroxide. The addition of 88.2 cc. of water to 500 cc. of the sodium hydroxide solution of the strength given above, will give a solution which contains 4.0 gm. of the hydroxide in 1,000 cc. of water.

477. To Prepare an Ammonia-Silver Solution.—Dissolve 3 gm. of silver nitrate in 30 cc. of ammonium

hydroxide, and add it to 30 cc. of water which contains 3 gm. of sodium hydroxide.

TABLE LX

478. Table of Atomic Weights:

	O = 16	H = 1		O = 16	H = 1
Aluminium.....	Al	27.1	Neodymium.....	Nd	143.6
Antimony.....	Sb	120.2	Neon.....	Ne	19.94
Argon.....	A	39.99	Nickel.....	Ni	58.7
Arsenic.....	As	75.0	Nitrogen.....	N	14.04
Barium.....	Ba	137.4	Osmium.....	Os	191.0
Bismuth.....	Bi	208.5	Oxygen.....	O	16.00
Boron.....	B	11.0	Palladium.....	Pd	106.5
Bromine.....	Br	79.96	Phosphorus.....	P	31.
Cadmium.....	Cd	112.4	Platinum.....	Pt	194.9
Caesium.....	Cs	133.0	Potassium.....	K	39.15
Calcium.....	Ca	40.1	Praseodymium.....	Pr	140.5
Carbon.....	C	12.0	Radium.....	Ra	226.
Cerium.....	Ce	140.0	Rhodium.....	Rh	103.0
Chlorine.....	Cl	35.45	Rubidium.....	Rb	85.4
Chromium.....	Cr	52.1	Ruthenium.....	Ru	101.7
Cobalt.....	Co	59.00	Samarium.....	Sm	150.
Columbium.....	Cb	94.	Scandium.....	Sc	44.1
Copper.....	Cu	63.6	Selenium.....	Se	79.2
Erbium.....	Er	168.0	Silicon.....	Si	28.4
Fluorine.....	Fl	19.00	Silver.....	Ag	107.93
Gadolinium.....	Gd	156.6	Sodium.....	Na	23.05
Gallium.....	Ga	70.00	Strontium.....	Sr	87.60
Germanium.....	Ge	72.5	Sulphur.....	S	32.06
Glucinum.....	Gl	9.1	Tantalum.....	Ta	183.
Gold.....	Au	197.2	Tellurium.....	Te	127.6
Helium.....	He	3.96	Terbium.....	Tr	160.0
Hydrogen.....	H	1.008	Thallium.....	Tl	204.15
Indium.....	In	114.1	Thorium.....	Th	232.
Iodine.....	I	126.85	Thulium.....	Tm	171.
Iridium.....	Ir	193.0	Tin.....	Sn	119.
Iron.....	Fe	55.9	Titanium.....	Ti	48.10
Krypton.....	Kr	81.76	Tungsten.....	W	184.
Lanthanum.....	La	138.9	Uranium.....	Ur	238.5
Lead.....	Pb	206.90	Vanadium.....	V	51.2
Lithium.....	Li	7.03	Xenon.....	Xe	128.
Magnesium.....	Mg	24.36	Ytterbium.....	Yb	173.
Manganese.....	Mn	55.0	Yttrium.....	Yt	89.
Mercury.....	Hg	200.	Zinc.....	Zn	65.4
Molybdenum.....	Mo	96.	Zirconium.....	Zr	90.6

INDEX

- Acetates, 270
- Acetic acid, 268.
 - glacial, 268
 - preparation, 268
 - salts, 270
- Acetylene, 353
 - burner, 353
 - flame, 353
 - preparation and properties, 353
- Acid, acetic, 268
 - arsenious, 236
 - arsenic, 237
 - antimonic, 239
 - boric, 317
 - butyric, 273
 - carbolic, 256
 - carbonic, 257
 - chloric, 196
 - glacial acetic, 268
 - hydriodic see Hydrogen iodide, 63
 - hydrobromic, 199
 - hydrochloric, see Hydrogen chloride, 58
 - hydrocyanic, 262
 - hydrofluoric, 192
 - hydroxides, 144
 - hypochlorous, 193
 - iodic, 200
 - metaphosphoric, 232
 - muriatic, see Hydrogen chloride, 58
 - nitric, 147, 225
 - nitrous, 224
 - Nordhausen sulphuric, 133
 - oleic, 271
 - orthophosphoric, 231
 - oxalic, 159, 415
 - palmitic, 270
 - perchloric, 197
 - periodic, 200
 - phosphoric, 231
 - phosphorus, 231
 - prussic, 262
 - pyrophosphoric, 231
- Acid, silicic, 294
 - stearic, 271
 - sulphocarbonic, 261
 - sulphuric, 207
 - sulphurous, 206
 - telluric, 215
 - tellurous, 215
- Acids defined, 155
 - general properties, 144, 155
 - naming, 164
 - and neutralization, 158, 159
- Action of chlorine on hydrogen, 57
- Air, composition, 65
 - a mixture, 66
- Albumens, 290
 - table, 291
- Alchemists, 25
- Alcohol, ethyl (grain), 265
 - constitution, 265
 - fermentation, 259
- Alcohols, 265
 - constitution, 265
 - diatomic, 265
 - monatomic, 265
 - triatomic, 265
- Aldehydes, 266
 - acetic, 266
 - formic, 267
- Alkali, action on litmus, 159
 - earth group of elements, 340
 - earth metals, 348
 - general properties, 355
 - group of elements, 359
 - hydroxides, 143
- Alkaline hydroxides, 143
 - action on litmus, 159
 - structure, 155
- Allotropic modifications, carbon, 32
 - sulphur, 124
 - phosphorus, 131
- Allotropy, and the constitution of gaseous molecules, 125
 - and weight of molecules of solids, 126
- Alloys, copper, 371
 - fusible, 344
 - lead, 303
 - nickel, 388
 - silver, 377
 - tin, 303
 - zinc, 371
- Alum, 322
 - ammonium, 322
 - chrome, 322
 - ferric, 322
 - potassium, 322
 - sodium, 322
- Aluminium, 317
 - chloride, 320
 - compounds 320
 - halogen derivatives, 320
 - hydroxide, 320
 - occurrence, 317
 - oxide, 320
 - preparation, 318
 - properties, 319
 - salts, 321
 - silicates, 322
 - sulphate, 321
 - uses, 319
- Ammonia, 68, 142, 219, 220
 - chemical properties, 221
 - composition, 69
 - formation, 399
 - from coal, 250, 255
 - ice-making, 220
 - oxidation, 399
 - preparation, 68
 - properties, 68
 - salts, 222
 - silver solution 416
 - water, 68, 221
- Ammonium, 222
 - alum, 322
 - chloride, 222
 - hydroxide 142
 - nitrate, 146, 227
 - salts, 222
- Amorphous, carbon, 33, 249
 - sulphur 124

- Analytic and synthetic change, 21
- Anhydride, acid, 165
- arsenious, 236
 - carbonic, 257
 - nitric, 165
 - nitrous, 165
 - sulphocarbonic, 261
 - sulphuric, 165
- Animal charcoal, 34
- Anode, 373
- Anthracite coal, 249
- Antimony, 237
- alloys, 303
 - as metalloid, 238, 239, 391
 - chloride, 238
 - compounds, 237
 - halogen derivatives, 238
 - hydrogen derivatives, 238
 - oxygen derivatives, 238
 - pentoxide, 239
 - preparation and properties, 237
 - trioxide, 238
- Appendix, 403
- Aqua ammoniac, 68
- Argentum, 92, 374
- Argon, 67, 417
- Armor plate, 388
- Arsenic, 233
- compounds, 234
 - detection, 234
 - halogen derivatives, 235
 - hydrogen derivatives, 234
 - Marsh's test, 234
 - occurrence, 233
 - oxygen derivatives, 236
 - pentoxide, 236
 - preparation, 233
 - properties, 234
 - trichloride, 235
 - trioxide, 236
- Arsenic acid, 237
- Arsenious acid, 236
- Arsine, 234
- Atmosphere, see Air, 65
- carbon dioxide in, 67
 - composition, 65, 67
 - ozone in, 83
- Atomic theory, 19, 98
- Atomic weights, 44, 417
- and multiple proportion, 97, 98
 - determination, 46, 50, 51, 52
 - table, 417
- Atoms, 19, 20, 21
- and dissociation, 186, 187
 - and molecules, 20
- Atoms, combining power, 98, 99
- Dalton's theory, 19, 98
 - persistence, 20
 - radio-active, 21
- Avogadro's law, 46, 78, 79
- density and, 78
 - determination, 78, 79
 - and formulas, 79
- Baby foods, 284
- table, 285
 - varieties, 285
- Bacillus mycoides, 399
- Bacteria, 399, 400, 401, 402
- ammonia producing, 399
 - in butter, 273
 - in clover roots, 401
 - in vinegar, 269
 - nitrifying, 399
 - nitroifying, 400
- Baking powder, 259
- Balances, 406
- Baking soda, 364
- Barium, 143, 353
- compounds, 354
 - dioxide, 354
 - halogen derivatives, 354
 - hydroxide, 143, 144, 354
 - monoxide, 354
 - occurrence, 143
 - oxygen derivatives, 354
 - properties, 143
 - sulphate, 355
- Bases, 171
- and acids, 122, 143, 144, 171, 172
 - and hydroxides compared, 171
 - origin, 122, 138, 140, 143
- Basic oxides, 138
- Beef fat, 272
- Beet sugar, 279
- Bessemer steel, 118
- Bicarbonate of soda, 364
- Bismuth, 239
- chloride, 240
 - compounds, 240
 - halogen derivatives, 240
 - nitrate, 241
 - oxygen derivatives, 240
 - pentoxide, 240
 - preparation and properties, 239
 - salts, 240
 - subnitrate, 241
 - trioxide, 240
- Bituminous coal, 249
- Black gunpowder, 227
- tin, 308
- Blast furnace, 114
- Bleaching cotton and linen, 195
- Bleaching powder, 194
- Blowpipe, 112
- Blowpipe flame, 112
- Blue, ultramarine, 327
- vitriol, 372
- Bonds, 21, 99, 100, 246
- Bone black, 34
- Bone meal, 232
- Borates, 317
- Borax, 317
- soldering, 317
 - sources, 317
- Boric acid, 317
- salts, borates, 317
- Boron, 315
- compounds, 316
 - halogen derivatives, 316
 - hydrogen derivatives, 316
 - occurrence, 315
 - oxygen derivatives, 316
 - properties, 315
 - trioxide, 316
- Boyle's law, 40, 412, 413
- proof of, 412, 413
- Brass, 371
- Bricks, 327
- Brimstone, 123
- Bromine, 198
- compounds, 199
 - occurrence, 198
 - oxides, 199
 - preparation and properties, 198
- Bronze, 371
- aluminium, 320
- Bunsen flame, 111
- Burette, 160, 406
- Burner, acetylene, 353
- Bunsen, 111
- Butane, 263
- Butter, 272
- artificial, 273
 - creamery, 273
 - rancid, 273
- Butyric acid, 273
- Cadmium, 344
- alloys, 344
 - properties and uses, 344
- Cæsium, 386
- Calcium, 138, 348

- Calcium, carbide, 247, 352
 - carbonate, 30, 140, 351
 - chloride, 349
 - halogen derivatives, 349
 - hydroxide, 142, 144, 350
 - hypochlorite, 193
 - oxides, 140, 349
 - phosphate, 232
 - preparation and properties, 138
- Calico printing, 334
- Calomel, 346
- Calorie, 177
- Candle flame, 113
- Cane sugar, 279
- Caramel, 283
- Carat, 382
- Carbide, calcium, 247, 352
 - iron, 261
- Carbohydrates, 278
 - modifications, 284
 - occurrence, 279
 - properties, 279
 - table, 278
- Carbon, 31, 32, 33, 35, 246
 - amorphous, 33, 249
 - chlorides, 256
 - compounds, 247
 - disulphide, 260
 - group of elements, 244
 - halogen derivatives, 256
 - hydrogen derivatives, 248
 - in carbon dioxide, 36
 - monoxide, 257
 - oxygen derivatives, 257
- Carbon dioxide, 30, 257
 - composition, 37
 - in air, 67
 - in effervescing waters, 258
 - in leavening mixtures, 259
 - occurrence, 66
 - preparation and properties, 30
- Carbonic acid, 257
 - salts, 257
- Carbon monoxide, 257
 - as reducing agent, 116
 - in water gas, 255
 - properties, 257
- Carborundum, 298, 299
- Carbureter, 254
- Carnallite, 137
- Cast iron, see Pig iron, 114
- Cathode, 370, 373
- Caustic, lime, 140, 349
 - potash, 142, 275, 276, 365
 - soda, 142, 275, 276, 361
- Cellulose, 286
 - modifications, 289
 - uses, 286
- Cements, 351
- Charcoal, 33
 - animal, 33, 34, 249
 - preparation, 31, 33, 249
 - properties, 31, 32, 34, 35
- Chemical change, 17, 18, 19
 - and energy, 174
 - and the atomic theory, 19
- Chemical energy, 175
- Chemical equivalents, 103, 104
- Chemistry and life, 398
- Chloral, 267
 - hydrate, 267
- Chili saltpeter, 365, 399
- Chloric acid, 196
 - salts, 197
- Chlorine, 54, 193
 - acids, 57, 194, 196, 197
 - and hydrogen, 57
 - bleaching power of, 56
 - commercial value of, 56
 - dioxide, 195
 - oxygen derivatives, 193
 - preparation, 54
 - properties, 55, 56
 - uses, 56, 194, 195
- Chloroform, 256
- Chlorophyll, 181
- Chromates, 332
- Chrome, alum, 322
 - iron, 330
- Chromic acid anhydride, 332
- Chromium, 330
 - chemical character, 334
 - chloride, 331
 - group of elements, 330
 - halogen derivatives, 331
 - occurrence, 330
 - oxygen derivatives, 331
 - properties, 330
 - salts, 332
 - trioxide, 331
- Cinnabar, 345
- Classification of elements, 391
- Clay, 326
- Coach varnish, 307
- Coal, origin, 249
 - anthracite, 249
 - bituminous, 249
 - composition, 249
 - distillation, 250
 - gas, 250, 251
- Coal, products from, 250, 255
 - soft, see Bituminous coal, 249
 - tar, 255
- Cobalt, 389
 - halogen derivatives, 389
 - oxygen derivatives, 389
 - cyanogen derivatives, 390
- Coins, gold, 382
 - nickel, 388
 - silver, 377
- Coke, 33, 251
- Colored glass, 296
- Combination of silver and chlorine in definite proportions, 92
 - silver and sulphur in definite proportions, 95
 - definite proportions, 97
- Combustion, 107, 108, 109
 - carbon in oxygen, 35
 - phosphorus in oxygen, 132
 - sodium in oxygen, 138
 - sulphur in oxygen, 132
 - sulphur dioxide in oxygen, 133
 - modern theory, 108, 109
 - phlogiston, 107
- Composition, air, 65
 - hydrogen sulphide, 29, 80
 - water by volume, 46
- Condenser coal gas, 251
 - Liebig's, 411
- Conservation, energy in chemical reactions, 174
 - matter, 20
- Converter, 118
- Copper, 368
 - alloys, 371
 - carbonate, see Malachite, 372
 - compounds, 372
 - electrolytic purification, 370
 - halogen derivatives, 372
 - nitrate, 372
 - occurrence, 368
 - ores, 368
 - oxygen derivatives, 48, 50
 - 372
 - preparation, 368
 - properties, 371
 - salts, 372
 - sulphate, 372
 - uses, 371
- Copperas, 387
- Cork stoppers, and their uses, 409

- Corrosive sublimate, 346
 Corundum, 320
 Cream of tartar, 259
 Cryolite, 318
 Cyanogen, 261
 and hydrogen, 262
 properties, 261
- Definition of chemistry, 11
 Definite proportions, 86, 97
 silver and chlorine, 92
 silver and sulphur, 95
- Density and atomic weight of elementary gas, 75
 and molecular weight of elementary gas, 76
 and two-volume law, 77
 and Avogadro's law, 78
 and molecular weight of compound gas, 77
- Destructive distillation, 250, 251
- Determination, atomic mass, 44, 46
 atomic weight of copper, 50
 atomic weight of oxygen, 46
 formula of hydrogen chloride, 58
 formulas, 54
- Developer, 378
- Dextrin, composition, 284
 preparation, 284
- Diamond, 32
- Dichromates, 333
- Diffusion, of gases, 38, 39
 solids in liquids, 15
- Disinfectant, corrosive sublimate 346
 formalin, 267
- Dissociation, by heat, 222
 and the theory of electrolysis, 186
 electrolytic, 184
- Distillation, coal, 250
 destructive, 250, 251
 petroleum, 264
 water, 411
 wood, 31
- Downward displacement, 55
- Drummond light, 350
- Drying oven, 403
- Dyads, 100
- Earthenware, 326
- Effervescence, 258
- Efflorescence, 364
- Electric furnace, 247, 318
- Electrodes, 45
- Electrolysis, acids, 150
 acid hydroxides, 151
 aluminium hydroxide, 318
 alkali hydroxides, 152
 alkali-earth hydroxides, 157
 common salt, 158
 copper compound, 156
 exothermic compounds, 183
 sodium hydroxide, 360
 theory, 186
 water, 44
- Electrolyte, 186
- Electromagnet, and how to make it, 412
- Electroplating, 373
- Electrotyping, 373
- Elements, 20, 22, 26
 acid properties, 393, 394
 basic properties, 393, 394
 classification, 391
 combine in definite and multiple proportion, 98
 necessary to plant life, 398
 table, 417
- Emery, 320
- Endothermic compounds, 176
 and foods, 182
 stability, 183
- Energy, 174
 chemical, 174
 expressed, 177, 178
 in molecules, 176
 mechanical, 174
 selective, 175
 transformed, 174
- Epsom salts, 341
- Essential properties, of iron, 12
 of lead, 12
 of simple and compound gases, 23
- Etching, 192
- Ethane, 262
- Ethyl alcohol, 265
- Evaporation, 403, 404, 410
- Exothermic compounds, 176
 stability, 183
- Families of elements, 394, 395
- Fats, 271
 composition, 271, 272
- Fatty acids, see Organic acids, 268
- Fermentation, acetic, 269
 alcoholic, 259
- Ferments, 259, 269, 284
- Ferric compounds, 384
 chloride, 384
 halogen derivatives, 384
 hydroxides, 385
 oxygen derivatives, 386
 salts, 387
- Ferrocyanide of potassium, 385
- Ferrocyanide of potassium, 385
- Fertilizer, 232
- Filter, charcoal, 34, 281
- Filtering process, 410
- Fixation of nitrogen, 400
- Flame, 111, 112, 113
 acetylene, 353
 Bunsen, 111
 hydrogen, 25, 26
 oxidizing, 111
 reducing, 111
- Flowers of sulphur, 123
- Fluorine, 191
 occurrence, 191
 preparation and properties, 191
- Food, 182
- Fool's gold, 387
- Formaldehyde, 267
- Formalin, 267
- Formation of ammonia, 399
- Formulas and definite proportions, 86
 multiple proportions, 91
- Furnace, blast, 114
 electric, 247, 318
 reverberatory, 120, 301
- Fusible alloys, 344
- Fusion, 411
- Galena, 301
- Galvanized iron, 343
- Gaps in periodic system, 395
- Gas, coal, 250
 effect of heat on volume, 41
 effect of pressure on volume, 40
 flame, 111
 illuminating, 250, 251, 253
 marsh, 248
 natural, 248
 water, 253
- Gases, combination by volume, 77, 78
 diffusion, 17, 38, 39
 general properties, 37

- Gasometer, 404
 General formula for neutralization, 162
 General structure of acid and alkaline hydroxides, 155
 Generator, hydrogen, 407
 hydrogen sulphide, 407
 water gas, 254
 Glacial acetic acid, 268
 Glass, 295
 blowing, 297
 Bohemian, 295
 colored, 296
 cut, 298
 flint, 298
 plate, 298
 preparation, 297
 tubes, 408
 water, 298
 window, 297
 Glazing pottery, 325
 Glover tower, 210
 Glucose, 282
 properties, 283
 Glycerides 271, 272
 Glycerine, 266
 Glyceryl, oleate, 272
 palmitate, 272
 stearate, 272
 Gold, 380
 alloys, 382
 chloride, 383
 coin, 382
 fool's, 387
 metallurgy, 380, 381
 occurrence, 380
 preparation, 380
 properties, 382
 purification, 382
 uses, 382
 Graduated flask, 405
 Graduating glass tubes, 411
 Gram, 405
 Grape sugar, 283
 properties, 283
 Graphite, 32, 247
 Green ultramarine, 327
 vitriol, 372
 Guncotton, 289
 preparation, 289
 properties, 290
 uses, 290
 Gunpowder, black, 227
 smokeless, 289
 Gypsum, 352
 Halogen group of elements, 191,
 201
 summary, 201, 202
 Hard coal, 249
 Hard water, 275
 Hematite, 113
 Homogeneity and mass, 13
 Hydraulic lime, 351
 Hydriodic acid, see Hydrogen
 iodide, 63
 Hydrocarbons, 263
 table, 264
 Hydrobromic acid, see Hydrogen
 bromide, 199
 Hydrochloric acid, see Hydrogen
 chloride, 58
 commercial, 363
 composition, 58
 Hydrocyanic acid, 262
 Hydrofluoric acid, 192
 salts, 193
 Hydrogen, 23, 24, 25
 chloride, 57, 58
 cyanide, 262
 dioxide, 354
 flame, 25
 in acids, 27, 151
 iodide, 63
 occurrence, 26
 peroxide, 354
 preparation, 23
 properties, 25
 Hydrogen sulphide, 29
 composition, 29, 79
 occurrence, 30
 preparation, 29
 properties, 30
 Hydroxides, acid, 144
 basic, 140, 141, 142, 145
 electrolysis, 152
 structure, 155
 Hypochlorous acid, 193
 salts, 193
 Ice-making, 220
 Illuminating gas, 250
 composition, 255
 preparation, 251, 253
 properties, 255
 Iodic acid, 200
 salts, 200
 Iodine, 62, 199
 compounds, 199
 detection, 63
 occurrence, 62
 Iodine oxides, 199
 pentoxide, 199
 preparation, 62
 properties, 63
 Ions, 186 —
 Ionization, 186
 Iron, cast, see Pig iron, 114, 115
 chlorides, 384
 compounds, 384
 cyanogen derivatives, 385
 galvanized, 343
 group of elements, 384
 halogen derivatives, 384
 hydroxides, 385
 malleable, 117, 120
 ores, 113
 oxygen derivatives, 386
 pig, 114
 preparation, 113
 properties, 113
 rust, 386
 salts, 387
 sulphides, 387
 Kaolin, 323
 analysis, 323
 Kerosene, 264
 Law, Boyle's, 40, 412
 of definite proportions, 86
 of multiple proportions, 91
 of octaves, 392
 periodic, 393
 Lead, 301
 alloys, 303
 chlorides, 304
 chromate, 333
 compounds, 303
 halogen derivatives, 303
 iodide, 304
 ore, 301
 oxygen derivatives, 304
 preparation, 301
 properties, 302
 salts, 305
 sugar of, 270
 uses, 303
 white, 305
 Leavening process, 259
 Le Blanc process for preparing
 sodium carbonate, 363
 Lignite, 249
 Lime, 349
 air-slaked, 350
 caustic, 349

- Lime chloride, 349
 light, 350
 milk, 350
 superphosphates, 232
 Limekiln, 349
 Limestone, 30, 349
 Limewater, 350
 Linseed oil, 308
 Litharge, see Lead monoxide, 304
 Lithium, 360
 occurrence and properties, 360
 Litmus, action on, acids, 159
 alkalis, 159
 salts, 159
 Luminosity of flame, 113
 Lunar caustic, 379

 Magnesium, 137, 340
 compounds, 341
 halogen derivatives, 340
 oxygen derivatives, 341
 preparation and properties, 137
 salts, 341
 sulphate, 341
 uses, 137, 138
 Malachite, 372
 Malleable iron, 117, 120
 Manganese, 335
 chemical character, 338
 compounds, 335
 halogen derivatives, 335
 oxygen derivatives, 335, 336
 occurrence, 335
 properties, 335
 Marsh gas, 248
 Marsh's test for arsenic, 234, 235
 Mass and chemical subdivision
 17
 and density 40
 and mechanical subdivision, 16
 Matches, 228
 Measuring liquids, 405
 Mercury, 345
 alloys, 345
 chlorides, 346
 compounds, 346
 fulminating, 347
 halogen derivatives, 346
 iodides, 346
 nitrates, 347
 oxygen derivatives, 347
 preparation, 345
 properties, 345
 red oxide, 347
 uses, 345

 Mercury, yellow oxide, 347
 Metalloids, 239, 391
 Metals, alkali, 359
 alkali-earth, 348
 classification, 391
 Metaphosphates, 232
 Metaphosphoric acid, 232
 Methane, occurrence, 248
 preparation, 248
 Methyl alcohol, 265
 Milk of lime, 350
 Minium, 304
 Molecular theory and the two-
 volume law, 80
 and nascent elements, 82
 Molecular weights, 75, 77
 and vapor density, 76, 77
 determination, 77, 126
 Mordants, 333
 uses, 334
 Mortar, 350
 Mucilage, 284
 Multiple proportions, 91
 and valence, 98
 Muriatic acid, 27, 58

 Naming of acids, bases, and salts,
 164
 Nascent elements, 82
 and ozone, 83
 Natural gas, 248
 Neutralization, 158
 and acids, bases, and salts, 163
 general formula, 162
 Nickel, 387
 alloys, 388
 chloride, 388
 coin, 388
 compounds, 388
 cyanogen derivatives, 389
 halogen derivatives, 388
 occurrence, 387
 oxygen derivatives, 388
 properties, 387
 steel, 388
 Nitric acid, 147, 225
 action on metals, 226
 composition, 165, 170, 226
 preparation, 147, 225
 properties, 226
 salts, 227
 Nitrifying bacteria, 399
 Nitrobacter, 400
 Nitrofying bacteria, 400
 Nitrogen, 63, 219

 Nitrogen family, 241, 242
 group of elements, 219
 halogen derivatives, 180, 222
 hydrogen derivatives, 219
 monoxide, 146, 223
 oxygen derivatives, 146, 222
 pentoxide, 223
 peroxide, 146, 223
 preparation, 63
 properties, 64
 rotation, 401
 trioxide, 147, 223
 Nitrosomonas, 399
 Nitrous acid, 224
 salts, 224

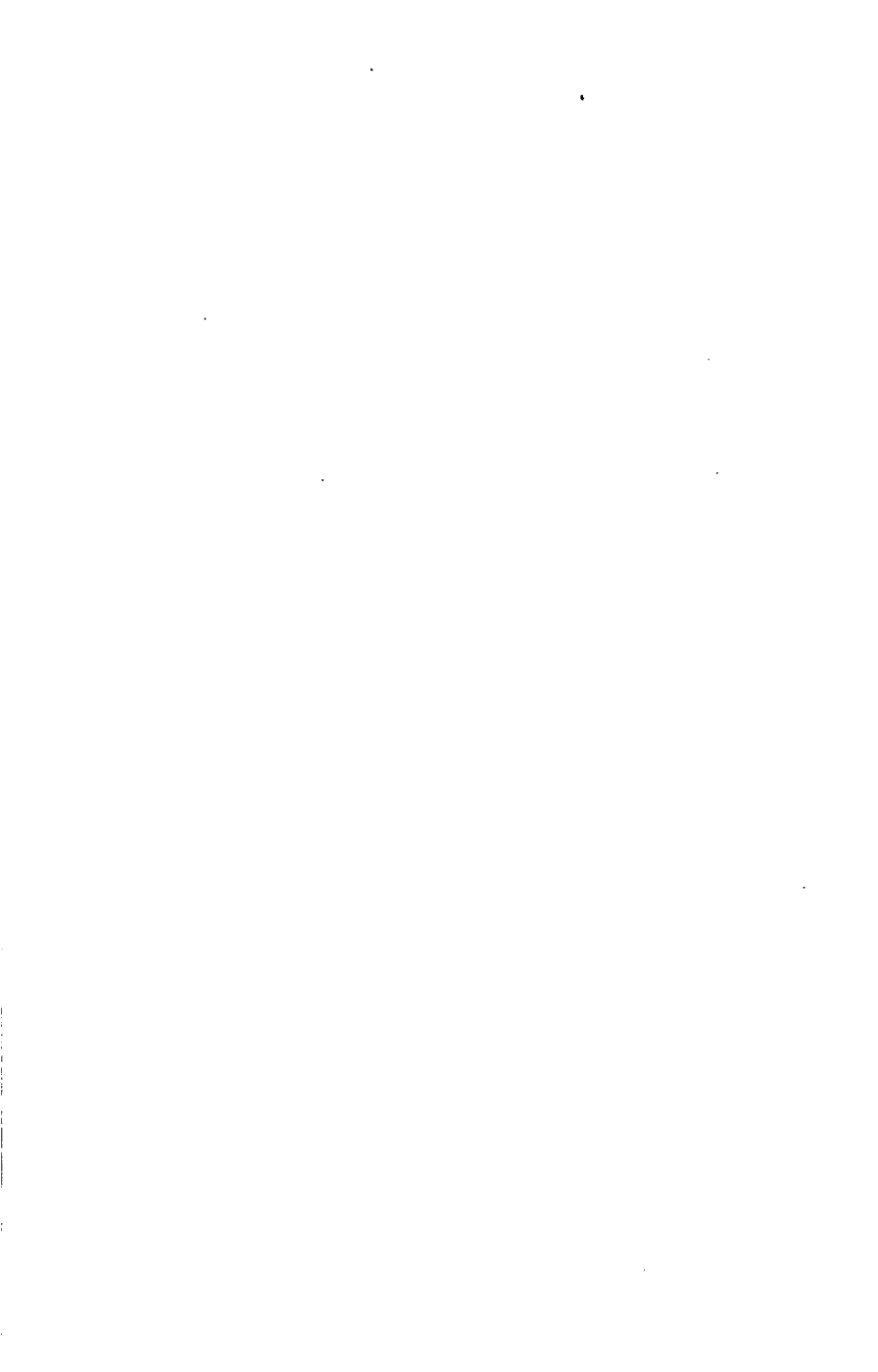
 Oil, lubricating, 264
 of vitriol, 372
 Oleic acid, 271
 Oleomargarine, 273
 Olive oil, 272
 Organic acids, 268
 composition, 268
 Orpiment, 233
 Orthophosphoric acid, 231
 Oxalic acid, 159, 160, 415
 Oxidation, 107
 and acids, 132, 134
 and alkalis, 138, 144
 and reduction in the prepara-
 tion of iron and steel, 113
 of foods, 182, 402
 Oxidation of metallic elements,
 138
 calcium, 140
 magnesium, 139
 potassium, 139
 sodium, 138
 Oxidizing agents, 110
 flame, 111
 Oxygen group of elements, 204
 summary, 216, 217
 Oxygen, 28
 occurrence, 29
 preparation, 28
 properties, 28
 relation to life, 29
 Ozone, 83
 preparation, 83
 structure, 84

 Paints and painting, 305
 Palmitic acid, 270
 Palm oil, 270
 Paper-making, 286, 287, 288

- Parchment, 289
 Paraffin, 264
 Paris green, 270
 Peat, 249
 Perchloric acid, 197
 Periodic acid, 200
 Periodic, law, 393
 table, 394
 uses, 396
 Permanganates, 337
 uses, 338
 Peroxide of hydrogen, 354
 Petroleum and its products, 264
 Pewter, 303
 Philosopher's stone, 25
 Phlogiston, 107
 Phosphates, 232
 Phosphine, 229
 Phosphonium compounds, 230
 Phosphoric acid, 231
 salts, 232
 Phosphorus, 129, 228
 combustion in oxygen, 132
 compounds, 229
 halogen derivatives, 230
 hydrogen derivatives, 229
 modifications, 131
 oxygen derivatives, 230
 pentoxide, 231
 preparation, 129
 properties, 130
 red, 131
 trichloride, 230
 trioxide, 230
 uses, 228
 yellow, 129, 130
 Photography, 378
 Photosynthesis, 180
 purpose of, 182
 Physical change, 16, 17
 Physical and chemical change
 compared, 22
 Physical properties of gases,
 37
 Pig iron, 114
 Pipette, 405
 Placer mining, 380
 Plaster of Paris, 352
 Plumbago, 32
 Pneumatic trough, 404
 Porcelain, 324
 manufacture, 324
 Portland cement, 351
 Potash, 365
 red prussiate, 385
 Potash, yellow prussiate, 385
 Potassium, 136, 364
 alum, 322
 chlorate, 197
 chromate, 332
 combustion in oxygen, 139
 compounds, 364
 cyanide, 261
 dichromate, 333
 ferricyanide, 385
 ferrocyanide, 385
 halogen derivatives, 364
 hydroxide, 365
 nitrate, 365
 Potassium, permanganate, 337
 properties, 136
 Pottery, 324
 Powder, gun, 227
 magnesium, 138
 smokeless, 289
 Preparation, barium hydroxide,
 143
 amorphous carbon, 33
 calcium hydroxide, 140
 carbon, 31
 chlorine, 54
 carbon dioxide, 30
 hydrogen sulphide, 29
 nitrogen, 63
 oxygen, 28
 strontium hydroxide, 143
 vinegar, 268
 wrought iron, 120
 Propane, 262
 Properties of atoms, 23
 carbon, 31
 carbon dioxide, 30
 charcoal, 33, 34, 35
 chlorine, 54
 hydrogen, 25
 hydrogen chloride, 58
 hydrogen sulphide, 30
 oxygen, 28
 phosphorus pentoxide, 134
 sulphur dioxide, 134
 sulphur trioxide, 134
 Prussian blue, 386
 Prussic acid, 262
 Puddling, 120
 Purple of Cassius, 383
 Pyrolusite, 335
 Pyrophosphoric acid, 231
 Quartz, 292
 Quicklime, 349
 Reaction, acid, 159
 alkaline, 159
 between acids and alkalis,
 158
 neutral, 159
 Realgar, 233
 Red fire, 355
 paint, 347, 386
 lead, 304
 Reducing agent, 111
 flame, 111
 Reduction, 110
 Relation of pressure to volume
 of gas, 40
 of volume to temperature of
 gas, 41
 of nitrogen to life, 65, 401,
 402
 density to atomic weight, 75
 valence and multiple propor-
 tion to oxidation and re-
 duction, 107
 oxidation to valence, 100
 reduction to valence, 110
 metallic and non-metallic ox-
 ides, 150, 155
 Roll sulphur, 123
 Rotation of nitrogen, 401
 Rouge, 386
 Rubidium, 366
 Ruby, 320
 Rusting of iron, 386
 Sal-soda, 364
 Salt, 163
 common, 134, 158
 Epsom, 341
 Saltpeter, 365
 Saponification, 275
 Scrubber, 251, 252
 Secondary phosphates, 232
 Selective energy, 175
 Selenium, 212
 chloride, 213
 compounds, 213
 dioxide, 213
 halogen derivatives, 213
 hydrogen derivatives, 213
 occurrence, 212, 213
 oxygen derivatives, 213
 preparation and properties,
 212, 213
 trioxide, 214
 Significance of chemical sub-
 division, 18

- Silicic acid, 294
 salts, silicates, 295
 Silicon, 292
 carbide, 298
 chloride, 293
 compounds, 293
 dioxide, 293
 halogen derivatives, 293
 hydrogen derivatives, 293
 occurrence, 292
 oxygen derivative, 293
 preparation and properties, 292
 tetrafluoride, 293
 Silicon disulphide, 298
 Silver, 374
 alloys, 377
 amalgamation process in extracting, 374, 375
 chloride, 92, 377
 coins, 377
 compounds, 377
 halogen derivatives, 377
 nitrate, 379
 occurrence, 374
 oxygen derivatives, 379
 preparation, 374, 375
 properties, 376
 salts, 379
 uses, 377
 Slaked lime, 350
 Smalt, 390
 Smokeless powder, 289
 Soap, 274
 hard, 275
 manufacture, 276
 soft, 275
 toilet, 278
 rosin, 288
 Soda, baking, 364
 water, 258
 Sodium, 134, 360
 alum, 322
 amalgam, 60
 bicarbonate, 364
 carbonate, 362, 364
 chloride, 134, 158
 combustion in oxygen, 138
 hydroxide, 140, 142, 361
 occurrence, 134
 preparation, 135, 360
 properties, 135, 360
 sulphate, 363
 Soft coal, 249
 Soluble glass, 298
 Solution of metallic oxides in water, 140
 Solvay process for preparation of sodium carbonate, 363
 Sources of nitrogen, 399
 Specific atomic weights, 51
 Stability of endothermic and exothermic compounds, 183
 Stamp mill, 374, 381
 Standard solution of oxalic acid, 415
 Standard solution of sodium hydrate, 416
 Starch, 283
 and malted foods, 284
 table, 284
 Stannic chloride, 309
 Stannic oxide, 310
 Stannous chloride, 309
 oxide, 310
 Stearic acid, 271
 Steel, manufacture, 116
 nickel, 388
 properties, 117
 uses, 120
 Sterling silver, 377
 Stibine, 238
 Stoneware, 326
 Stove polish, 32, 247
 Strontium, 143, 355
 preparation and properties, 143, 355
 uses, 355
 Structure of metallic and non-metallic oxides, 150, 155
 Sublimate, corrosive, 346
 Subnitrate of bismuth, 241
 Substitution, 166
 general formula for, 171
 Sugar, 278, 279
 manufacture, 279, 280
 Sulphocarbonic acid, 261
 salts, 261
 Sulphur, 122, 204
 allotropic modifications, 124
 chloride, 206
 compounds, 205
 dioxide, 132, 206
 flowers of, 123
 halogen derivatives, 205
 hydrogen derivative, 205
 occurrence, 122
 oxygen derivatives, 206
 preparation, 122
 properties, 123
 Sulphur, trioxide, 133, 206, 415
 uses, 123
 Sulphuretted hydrogen, 29, 205
 Sulphuric acid, 207
 chemical process in making, 210
 concentrated, 211
 manufacture, 209
 Nordhausen, 133
 preparation in laboratory, 208
 properties, 211
 salts, 212
 uses, 207
 Sulphurous acid, 206
 salts, 207
 Sunlight and photosynthesis, 180
 Superheater, 254
 Superphosphate, 232
 Synthesis of endothermic compounds, 180
 Table of atomic weights, 417
 Tallow, 271, 272
 Tar, 255
 Tellurium, 214
 compounds, 214
 dioxide, 214
 halogen derivatives, 214
 hydrogen derivative, 214
 occurrence, 214
 oxygen derivatives, 214
 properties, 214
 trioxide, 215
 Telluric acid, 215
 Tellurous acid, 215
 Theory, atomic, 19, 20, 21
 electrolysis, 186
 Thermal equation, 177, 178
 Thermometers, 403
 Thomas-Gilchrist process in making steel, 120
 Tin, 308
 alloys, 371
 amalgam, 345
 block, 308
 chlorides, 309
 compounds, 309
 dioxide, 310
 halogen derivatives, 309
 monoxide, 310
 occurrence and preparation, 308
 oxygen derivatives, 310

- Tin**, properties, 308
stone, 308
uses, 309
- To ascertain the volume of a gas at 0° temperature**, 414
- To ascertain the volume of a gas at 760 mm. pressure**, 414
- To ascertain the volume of a gas at 0° and 760 mm. pressure**, 414
- Turnbull's blue**, 385
- Tuyeres**, 114
- Two-volume law and molecular theory of gases**, 80
- Type metal**, 303
- Types of coal**, 249
- Ultramarine**, 327
- Urea**, 402
- Uses of the periodic law**, 396
- Valence**, 99
and the structure of molecules, 100
and compounds, 102
and equivalent quantities, 103
- Valence, variation in**, 101
- Varieties of carbon** 32
- Varnish**, 306
- Vaseline**, 264
- Vein mining**, 380
- Verdigris**, 270
- Vermilion**, 347
- Vinegar**, 268
preparation, 268
rapid process, 269
- Vitriol, blue**, 372
green, 387
oil of, see Sulphuric acid, 211, 212
white, 344
- Water-bath**, 403
- Water, carbonated**, 258
composition, 46
electrolysis, 44
gas, 253
glass, 298
soda, 258
- Weighing solids**, 406
- Welding iron**, 117
- White, lead**, 305
paint 305, 343
- White vitriol**, 344
zinc, 343
- Wood, alcohol. see Methyl alcohol**, 265
charcoal, 31, 34, 35
composition, 249
- Wrought iron**, 120
- Yeast, in bread-making**, 259
- Yellow paint**, 333
- Zinc**, 341
alloys, 371
chloride, 343
compounds, 343
dust, 342
halogen derivatives, 343
iodide, 343
ores, 341
occurrence, 341
oxygen derivatives, 343
preparation, 341
properties, 342
salts, 344
sulphate, 344
uses, 343
white, 343



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